PB81-232290

Determination of Haloethers in Industrial and Municipal Wastewaters

Monsanto Research Corp.
Dayton, OH

Prepared for

Environmental Monitoring and Support Lab.
Cincinnati, OH

Jul 81

U.S. Department of Commerce
National Technical Information Service
NTIS

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/4-81-062	2. ORD Report
3. RECIPIENT'S ACCESSION NO. PB82 129229
4. TITLE AND SUBTITLE DETERMINATION OF HALOETHERS IN INDUSTRIAL AND MUNICIPAL WASTEWATERS	5. REPORT DATE July 1981
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Paul L. Sherman, Joseph M. Kyne, Roger C. Gable, John V. Pustinger, and Carl R. McMillin	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Monsanto Research Corporation 1515 Nicholas Road Dayton, Ohio 45407	10. PROGRAM ELEMENT NO. 1BD612 11. CONTRACT/GRANT NO. 68-03-2633
12. SPONSORING AGENCY NAME AND ADDRESS Environmental Monitoring and Support Laboratory Office of Research and Development U.S. Environmental Protection Agency Cincinnati, Ohio 45268	13. TYPE OF REPORT AND PERIOD COVERED Final - 10/25/77-12/31/78 14. SPONSORING AGENCY CODE EPA/600/06
15. SUPPLEMENTARY NOTES	

16. ABSTRACT

This document describes an analytical method, not based on mass spectrometry, for the analysis of haloethers in water and wastewater.

The following haloethers were originally included in this study: 2-chloroethyl vinyl ether, bis(2-chloroisopropyl) ether, bis(2-chloroethyl) ether, bis(2-chloroethoxy) methane, 4-chlorophenyl phenyl ether, 4-bromophenyl phenyl ether, and (bischloromethyl) ether. The 2-chloroethyl vinyl ether and the bis(chloromethyl) ether were later deleted from the project because of extreme volatility and hydrolytic instability, respectively.

Gas chromatography studies were completed to compare different packings for use with haloethers and to compare the results obtained using a Hall electrolytic conductivity detection with those obtained using an electron capture detector. Various solvents were evaluated for use in extracting haloethers from wastewater. Sample preservation was studied at various pH and residual chlorine levels and different temperatures. The stability of haloethers stored in acetone and in methanol was observed. Chromatographic cleanup procedures were investigated for the removal of potential interferences.

The workable method developed in this program for the analysis of haloethers in wastewater consisted of a liquid/liquid extraction using methylene chloride, an evaporation step using Kuderna-Danish (K-D) evaporators, a column chromatographic cleanup procedure using Florisil, another K-D evaporation of the fraction from the Florisil column, and subsequent analysis by gas chromatography using an electrolytic conductivity detector.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Haloethers Gas chromatography Preservation Water analysis Industrial wastes	Priority Pollutants	

18. DISTRIBUTION STATEMENT Release to Public	19. SECURITY CLASS (This Report) UNCLASSIFIED	21. NO. OF PAGES 78
	20. SECURITY CLASS (This page) UNCLASSIFIED	22. PRICE

EPA Form 2220-1 (9-73)

CLASSIFICATION

PB81-232290

ELITE
PICA

EPA-600/4-81-062
July 1981

DETERMINATION OF HALOETHERS IN INDUSTRIAL AND MUNICIPAL WASTEWATERS

by

Paul L. Sherman, Joseph M. Kyne, Roger C. Gable,
John V. Pustinger, and Carl R. McMillin
Monsanto Research Corporation
Dayton, Ohio 45407

Contract No. 68-03-2633

Project Officer

James Longbottom
Physical and Chemical Methods Branch
Environmental Monitoring and Support Laboratory
Cincinnati, Ohio 45268

SIX TYPING LINES REMAIN

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

LAST LINE

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA 22161

CLASSIFICATION

DISCLAIMER

This report has been reviewed by the Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

CLASSIFICATION

CLASSIFICATION

FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory-Cincinnati conducts research to:

- Develop and evaluate techniques to measure the presence and concentration of physical, chemical, and radiological pollutants in water, wastewater, bottom sediments, and solid waste.
- Investigate methods for the concentration, recovery, and identification of viruses, bacteria, and other microbiological organisms in water. Conduct studies to determine the responses of aquatic organisms to water quality.
- Conduct an Agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and wastewater.

Under provisions of the Clean Water Act, the Environmental Protection Agency is required to promulgate guidelines establishing test procedures for the analysis of pollutants. The Clean Water Act Amendments of 1977 emphasize the control of toxic pollutants and declare the 65 "priority" pollutants and classes of pollutants to be toxic under Section 307(a) of the Act. This report is one of a series that investigate the analytical behavior of selected priority pollutants and suggests a suitable test procedure for their measurement.

R. L. Booth

Robert L. Booth
Acting Director
Environmental Monitoring and Support Laboratory

SIX TYPING LINES REMAIN
LAST LINE

CLASSIFICATION

ABSTRACT

This document describes an analytical method, not based on mass spectrometry, for the analysis of haloethers in water and wastewater.

The following haloethers were originally included in this study: 2-chloroethyl vinyl ether, bis(2-chloroisopropyl) ether, bis (2-chloroethyl) ether, bis(2-chloroethoxy) methane, 4-chlorophenyl phenyl ether, 4-bromophenyl phenyl ether, and (bischloromethyl) ether. The 2-chloroethyl vinyl ether and the bis(chloromethyl) ether were later deleted from the project because of extreme volatility and hydrolytic instability, respectively.

A literature search was conducted to acquire published information on the hydrolytic stability of the haloethers, methods for the detection of haloethers in water, and methods for the isolation, concentration, and analysis of haloethers. Gas chromatography studies were completed to compare different packings for use with haloethers and to compare the results obtained using a Hall electrolytic conductivity detection with those obtained using an electron capture detector. Various solvents were evaluated for use in extracting haloethers from wastewater. Sample preservation was studied at various pH and residual chlorine levels and different temperatures. The stability of haloethers stored in acetone and in methanol was observed. Chromatographic cleanup procedures were investigated for the removal of potential interferences.

The workable method developed in this program for the analysis of haloethers in wastewater consisted of a liquid/liquid extraction using methylene chloride, an evaporation step using Kuderna-Danish (K-D) evaporators, a column chromatographic cleanup procedure using Florisil, another K-D evaporation of the fraction from the Florisil column, and subsequent analysis by gas chromatography using an electrolytic conductivity detector.

This report was submitted in partial fulfillment of Contract No. 68-03-2033 by Monsanto Research Corporation under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period 25 October 1977 through 31 December 1978.

CONTENTS

	Page
Foreword	iii
Abstract	iv
Figures	vi
Tables	vii
1. Introduction	1
2. Summary	2
3. Haloethers literature review	4
Introduction	4
Hydrolytic stability	5
Detection of haloethers in water	10
Methods for the isolation, concentration, and analysis of haloethers	11
4. Gas Chromatography Studies	18
Columns and conditions	18
Initial detector studies	23
5. Extraction Studies	29
Extraction at pH 2	29
Extraction at pH 7	30
Extraction at pH 10	30
6. Preservation Studies	34
Preparation	34
Results	34
7. Solvent Stability Studies	37
8. Resin Studies	44
9. Column Chromatography Studies	47
Column packed with Florisil	47
Column packed with silica gel	48
10. Application of Method to Wastewater Samples	53
References	59
Appendices	
A. Method for Sampling and Analysis	63
B. Standardization of Florisil	69

FIGURES

Number		Page
1	Chromatogram of haloethers on column packed with SP-1000 on Supelcoport and using flame ionization detector.	20
2	Chromatogram of haloethers on column packed with SP-100 on Supelcoport and using Hall electrolytic conductivity detector.	20
3	Chromatogram of haloethers on column packed with Tenax-GC and using flame ionization detector . . .	21
4	Chromatogram of haloethers on column packed with Tenax-GC and using Hall electrolyte conductivity detector	21
5	Chromatogram of haloethers with new conditions . . .	23
6	Calibration curve for CPPE	24
7	Chromatogram of BCIPE on column packed with SP-1000 and detected simultaneously using FID and electron capture detectors, showing electron-capture impurities	25
8	Chromatogram of haloethers on column packed with SP-1000 and detected using an electron capture detector	25
9	Chromatogram of haloethers on the modified Hall Model 700 detector	27
10	Chromatogram showing the response of BCME in comparison to three other haloethers on column packed with SP-1000 on Supelcoport	28
11	Typical chromatogram for CEVE with purge and trap system.	33

TABLES

Number		Page
1	Haloethers in this Study.	4
2	Amount of BCME Formed at 40% Relative Humidity and 26°C at Various CH_2O/HCl Concentrations in Air. .	7
3	Amount of BCME Formed at Various Relative Humidities and Room Temperature at Various CH_2O/HCl Concentrations in Air	8
4	Hydrolysis Half-Life of BCME in Humid Air	8
5	Hydrolysis of Bis(chloromethy) Ether in Water and Aqueous HCl and NaOH.	10
6	Haloethers Detected in Water.	12
7	Analysis of Haloethers in Air with Porous Polymer Absorber/Gas Chromatography/Mass Spectrometry . .	14
8	Derivative Formation for Analysis of BCME in Air. .	16
9	Analysis of Haloethers in Water	17
10	Haloether Chromatographic Conditions for Columns Packed with SP-1000 or Tenax-GC	19
11	Retention Times of Haloethers on Two GC Columns Relative to Aldrin.	19
12	New Haloether Chromatographic Conditions for Column Packed with SP-1000.	22
13	Haloether Chromatographic Conditions for Column Packed with SP-1000 and Using Electron Capture Detector.	24
14	Sensitivity for Haloethers.	26
15	Reproducibility Data.	27
16	Results of Extraction Studies	31
17	Results of Anova for Solvent Extraction Studies . .	31
18	Conditions for GC/MS Analysis of CEVE	32
19	Percent Recovery for CEVE	32
20	Preservation Study Results.	35
21	Results of Anova Analysis of Preservation Study Results	36
22	Average Recovery (%) of Haloethers from Preservation Study Samples at Neutral and Basic pH	36
23	Concentrations of Solvent Solutions	37
24	Concentrations of Standards	38
25	Haloether Chromatographic Conditions with Electron Capture Detector.	38
26	Concentration of Initial Methanol Solution Used for Solvent Stability Study	38

TABLES (continued)

Number		Page
27	Concentration of Initial Acetone Solution Used for Solvent Stability Study.	39
28	Results of Analysis of Methanol Solution After Storage for 30 Days.	39
29	Results of Analysis of Acetone Solution After Storage for 30 Days.	40
30	Results of Analysis of Methanol Solution After Storage for 60 Days.	40
31	Results of Analysis of Acetone Solution After Storage for 60 Days.	41
32	Results of Analysis of Methanol Solution After Storage for 90 Days.	41
33	Results of Analysis for Acetone Solution After Storage for 90 Days.	42
34	Comparison of All Storage Times.	42
35	Statistical Data for XAD-2 Resin at pH 2	44
36	Statistical Data for XAD-2 Resin at pH 7	45
37	Statistical Data for XAD-2 at pH 10.	45
38	Average Recovery Percent (Three Detectors) of Haloethers on Chromatographic Column Packed with Florisil and Eluted with 200 mL 6% Ethyl Ether in Petroleum Ether	47
39	Recovery of Haloethers on Chromatographic Column Packed with Silica Gel and Eluted with Methylene Chloride in Hexane - First FID Analysis.	49
40	Recovery of Haloethers on Chromatographic Column Packed with Silica Gel and Eluted with Methylene Chloride in Hexane - Second FID Analysis	50
41	Recovery of Haloethers on Chromatographic Column Packed with Silica Gel and Eluted with Methylene Chloride in Hexane - Third FID Analysis.	51
42	Recovery of Haloethers on Chromatographic Column Packed with Silica Gel and Eluted with Methylene Chloride in Hexane - (Hall Model 700).	52
43	Distribution of Wastewater Sample Portions	53
44	Concentration of Haloethers in Spiking Solution. . .	53
45	Recovery of Haloethers from Wastewater from Municipal Secondary Waste Treatment Plant Using Column Packed with SP-1000 and Hall Electrolytic Conductivity Detector.	54
46	Average Results for Five Analyses of Haloether Standard Analyzed on Column Packed with SP-1000 and Using Hall Electrolytic Conductivity Detector.	55
47	Percent Recoveries of Haloethers from Industrial and Municipal Wastewater (Determined by Peak Amplitude) Using Column Packed with SP-1000 and Hall Electrolytic Detector (Average of Three Samples).	56
48	"t" Values for Three Sets of Wastewater Samples. . .	57

CLASSIFICATION

SECTION 1

INTRODUCTION

This report describes work completed on EPA contract 68-03-2633, "Development and Application of Test Procedures for Specific Toxic Substances in Wastewater, Category 2: Haloethers." The objective of this program is to develop a method for the analysis of haloehters in water and wastewater which does not involve mass spectrometry.

The following haloethers were included in this study: 2-chloroethyl vinyl ether (CEVE), bis(2-chloroisopropyl) ether (BCIPE), bi(2-chloroethyl) ether (BCEE), bis(2-chloroethoxy) methane (BCEXM), 4-chlorophenyl phenyl ether (CPPE), and 4-bromophenyl phenyl ether (BPPE). Bis(chloromethyl) ether (BCME) was originally included in this category; however, due to its hydrolytic instability, BCME was removed from this study, but its chromatographic retention time was determined under the same conditions as the other six haloethers.

The following studies were included in this project: a literature review, gas chromatography, solvent stability, sample extraction and preservation, column chromatography, resin performance, and the application of the analytical technique to actual wastewater samples. Accomplishments are summarized in Section 2. Detailed description of all studies are provided in Sections 3 through 10 of this report.

SIX TYPING LINES REMAIN

LAST LINE

CLASSIFICATION

CLASSIFICATION

SECTION 2

SUMMARY

The objective of this study is to develop a method for the analysis of haloethers in water and wastewater that does not involve mass spectrometry (GC/MS). The method developed involves sample extraction, cleanup, and analysis by gas chromatography with an electrolytic conductivity detector. This category originally included seven compounds: chloroethyl vinyl ether (CEVE), bis (2-chloroisopropyl) ether (BCIPE), bis(2-chloroethyl) ether (BCEE), bis(2-chloroethoxy) methane (BCEXM), bis(chloromethyl) ether (BCME), 4-chlorophenyl phenyl ether (CPPE), and 4-bromophenyl phenyl ether (BPPE). BCME and CEVE were subsequently removed from the list, the former because of its hydrolytic instability in water, and the latter because of its extreme volatility.

Two gas chromatographic packings were compared for best results with these haloethers. The 3% SP-1000 on Supelcoport was found to be superior to Tenax-GC because of better peak shape and resolution. Comparison of the Hall electrolytic conductivity detector with the electron capture detector showed the Hall detector to be the better choice because of its specificity. The Hall detector also has better reproducibility and lower detection limits for the haloethers.

Studies were completed to determine the best methods for sample extraction and preservation, including resin sampling. A solvent stability study was also conducted. The following solvents were evaluated for the extraction of haloethers from wastewater: methylene chloride, 15% ethyl ether in hexane, and pentane. For this liquid/liquid extraction, methylene chloride proved to be the best extracting solvent.

The possible use of Ambersorb XE-340 and XAD-2 resins for sample collection was also studied. Very little difference was found between the liquid/liquid extraction and the resin sorption methods. The average percent recovery for the four haloethers (BCIPE, BCEE, BCEXM, and BPPE) was 67% using resin sorption and 68.3% using liquid/liquid extraction. While there seemed to be little difference between the direct sampling parameters (pH, temperature, and residual chlorine), the XAD-2 was definitely the better choice of sampling resin because the haloethers could not be stripped from the Ambersorb XE-340 resin.

CLASSIFICATION

Sample preservation was determined at three different pH levels (2, 7, and 10) and with residual chlorine levels of 0 ppm and 2 ppm using temperatures of 0°C and 25°C. A study was also completed to compare the storage stability of the haloethers in acetone and methanol. Samples of the haloethers in these water miscible solvents were stored in flame-sealed glass ampules under normal laboratory conditions for periods of 30, 60, and 90 days. CEVE was found to be very unstable in methanol, but the other five haloethers were very stable in both solvents.

Two chromatographic cleanup procedures involving silica gel and Florisil were investigated for the removal of potential interferences in actual wastewater samples. Column chromatography on silica gel yielded very erratic and irreproducible results, but the Florisil cleanup procedure produced very stable and acceptable results.

A study was performed to determine the validity of the analytical method developed for application to actual wastewaters. Four samples were obtained, one from a municipal source and three from industrial sources. The samples were spiked, extracted, evaporated, column chromatographed, and evaporated again before analysis by gas chromatography with an electrolytic conductivity detector. One of the industrial effluent extracts was too complex for analysis using extraction and column chromatographic methods developed during this project. A "t" test was performed on the data from these four sets of samples. The only significant difference in recovery occurred between samples extracted and those processed by resin sorption; resin sorption yielded better recovery for the two industrial samples.

All of the aforementioned studies led to the development of an actual workable method for the analysis of wastewater. This method involved a liquid/liquid extraction using methylene chloride, an evaporation step using Kuderna-Danish (K-D) evaporators, a column chromatographic cleanup procedure using Florisil, another K-D evaporation of the fraction from the Florisil column, and subsequent analysis by gas chromatography using an electrolytic conductivity detector.

SIX TYPING LINES REMAIN

LAST LINE

CLASSIFICATION

SECTION 3

HALOETHERS LITERATURE REVIEW

INTRODUCTION

A review of literature pertinent to the seven haloethers included in this program was conducted during November 1977, prior to the preliminary contract meeting. The seven haloethers of interest and their abbreviations are listed in Table 1. Information in this report was gathered from a literature search performed by MRC in 1976 on EPA contract 68-01-1980, a literature review of haloethers conducted by Syracuse University in 1975 (1), and a computerized literature search of three commercial search services, the National Library of Medicine, System Development Corporation, and Lockheed Information Systems. These information sources provided coverage of all scientific literature in this report through approximately 15 November 1977. The main topics discussed in the following sections are hydrolytic stability of haloethers, reports of detection of haloethers in water, and methods for the isolation, concentration and analysis of haloethers.

TABLE 1. HALOETHERS IN THIS STUDY

Compound	Abbreviation
Bis(chloromethyl) ether	BCME
2-Chloroethyl vinyl ether	CEVE
Bis(2-chloroethyl) ether	BCEE
Bis(2-chloroisopropyl) ether	BCIPE
Bis(2-chloroethoxy) methane	BCEXM
4-Chlorophenyl phenyl ether	CPPE
4-Bromophenyl phenyl ether	BPPE

SIX TYPING LINES REMAIN

(1) Durkin, P. R., P. H. Howard, and J. Saxena. Investigation of Selected Potential Environmental Contaminants: Haloethers. EPA 560/2-75-006, U.S. Environmental Protection Agency, Washington, D.C., September 1975. 178 pp.

CLASSIFICATION

CLASSIFICATION

HYDROLYTIC STABILITY

Literature related to the hydrolytic stability of chloroethers can be divided into two types: 1) information related to all of the ethers except BCME, and 2) data related to BCME. These types are discussed separately below.

Haloethers Other Than BCME

Böhme and Sell (2) measured the hydrolysis rate of BCEE in a dioxane-water mixture (20M water in dioxane) at 100°C. The half-life for BCEE under these conditions was 12.8 days. Van Duuren and co-workers (3) measured the kinetics of the hydrolysis of microliter quantities of six chloroethers in 10 mL of a water-formaldehyde (3:1) solution. The hydrochloric acid formed was titrated with an automatic recording titrator. The half-life of all ethers with alpha-chloro substituents was found to be less than 2 minutes, and the half-life of ethers with no alpha-chloro substitution was greater than 23 hours. The half-life of BCME was listed in this study as less than 2 minutes and that of BCEE as greater than 23 hours. Salomaa and associates (4) have studied the hydrolysis of chlorovinyl eithers and chloro-substituted acetals under acid conditions. They found that chlorovinyl ethers, such as chloroethyl vinyl ether, are readily hydrolyzed to an aldehyde and alcohol as shown in Equation 1.

$$ClCH_2CH_2\text{-}O\text{-}CH{=}CH_2 \xrightarrow{H_3O^+} ClCH_2CH_2OH + CH_3\text{-}\overset{\overset{O}{\|}}{C}\text{-}H \qquad (1)$$

Their equations for two hydrolysis pathways for chloro-substituted acetals are shown below:

$$ClCH_2CH_2OCH_2\ OCH_2CH_3 \xrightarrow{H^+} ClCH_2CH_2\overset{+}{O}{=}CH_2 + HOCH_2CH_3 \qquad (2)$$

$$ClCH_2CH_2\ OCH_2OCH_2CH_3 \xrightarrow{H^+} ClCH_2CH_2OH + CH_2{=}OCH_2CH_3 \qquad (3)$$

---

(2) Böhme, H. and K. Sell. The Hydrolysis of Halogenated Ethers and Thio Ethers in Water-Dioxane Mixtures. Chem. Ber., 81:123-130, 1973.

(3) Van Duuren, B. L., C. Katz, B. M. Goldschmidt, K. Frenkel, and A. Sivak. Carcinogenicity of Halo-ethers. II. Structure - Activity Relation of Analogs of Bis(chloromethyl) ether. J. Nat. Cancer Inst., 48:1431-1439, 1972.

(4) Salomaa, P., A. Kankaanpera, and M. Lajuneh. Protolytic Cleavage of Vinyl Ethers. General Acid Catalysis, Structural Effects and Deuterium Solvent Isotope Effects. Acta. Chem. Scand., 20(7):1790-1801, 1966.

CLASSIFICATION

CLASSIFICATION

As part of a hazard priority ranking program for the National Science Foundation, Stanford Research Institute (5) predicted a half-life of 38.2 days for BCEE in water at a pH of 7. One other process for the catalytic cleavage of BCIPE, based on a patent by Dow Chemical Company, is shown below (6):

$$(ClCH_2CH[CH_3])_2O \xrightarrow[ZnCl_2]{HCl} CH_3\text{-}\underset{Cl}{CH}\text{-}CH_2Cl \text{ and } CH_3\text{-}\underset{OH}{CH}\text{-}CH_2Cl \qquad (4)$$

Bis(chloromethyl) Ether

The hydrolysis of BCME has been studied very extensively during the past ten years. Because BCME had been found to be a very potent carcinogen, the hydrolysis mechanism has been studied as a possible pathway for the destruction of the compound. Van Duuren, et al, (7, 8) reported that BCME reaches an equilibrium with its hydrolysis products, formaldehyde (CH_2O) and hydrogen chloride (HCl), in aqueous solutions as shown in Equation 5.

$$ClCH_2OCH_2Cl \underset{}{\overset{H_2O}{\rightleftharpoons}} HCH(=O) + HCl \qquad (5)$$

Where this hydrolysis was studied in heavy water (D_2O) (7), approximately 70% of the BCME was hydrolyzed in 2 minutes, and 80% after 18 hours according to the Van Duuren study. A number of other subsequent studies have explored the formation of BCME from HCl and formaldehyde in air or water and the hydrolysis of BCME in moist air or water. The status of hydrolysis studies in air are discussed below, followed by a discussion of hydrolysis studies in aqueous environments.

---

(5) Brown, S. L., F. Y. Chan, J. L. Jones, D. H. Liu, K. E. McCaleb, T. Mill, K. N. Sapios, and D. E. Schendal. Research Program on Hazard Priority Ranking of Manufactured Chemicals (Chemicals 61-79). NSF-RA-E-75-190D, National Science Foundation, Washington, D.C., April 1975. 198 pp.

(6) Roberts, R. F., Jr. Catalytically Cleaving Dichloro-isopropyl Ether. U.S. Patent 3,723,544 (to Dow Chemical Co.), 27 March 1973.

(7) Van Duuren, B. L., A. Sivak, B. M. Goldschmidt, C. Katz, and S. Melchionne. Carcinogenicity of Halo-ethers. J. Nat. Cancer Inst., 43:481, 1969.

(8) Van Duuren, B. L. Carcinogenic Epoxides, Lactones and Halo-ethers and Their Mode of Action. Ann. New YOrk Acad. Sci. 163:633-651, 1969.

CLASSIFICATION

CLASSIFICATION

The results of Van Duuren, et al, essentially went unnoticed with regard to their potential for the formation of BCME from HCl and formaldehyde or their potential for the incomplete hydrolysis of BCME (as indicated by only 80% hydrolysis after 18 hours). In 1973, Rohm and Haas Company (9) preliminarily announced that part-per-billion (ppb) levels of BCME may be formed in humid air from low levels of HCl and formaldehyde (5 ppm and 2 ppm, respectively). Subsequent studies by Frankel, et al., of Rohm and Haas (10) and by Kallos and Solomon of Dow Chemical Company (11) found that the potential was not as great as had been initially believed. Results of the Frankel Study are shown in Table 2.

TABLE 2. AMOUNT OF BCME FORMED AT 40% RELATIVE HUMIDITY AND 26°C AT VARIOUS CH_2O/HCl CONCENTRATIONS IN AIR (10)

CH_2O/HCl, ppm/ppm	BCME, ppb
4,000/40,000	5,000
1,000/10,000	730
1,000/1,000	130
300/300	23
100/100	3
20/20	<0.5 (limit of detection)

In the Kallos and Solomon study, BCME was found to be formed in five of 18 sample mixtures of HCl and CH_2O as shown in Table 3. The reactant concentrations in both studies in which detectable BCME was formed were greater than can be tolerated by humans. One reason for the concern about the formulation of BCME from CH_2O and HCl in air is the relatively long half-life of BCME in

(9) Bis(chloromethyl) Ether Can Form Spontaneously. Chem. Eng. News, 51(2):13, 8 January 1973.

(10) Frankel, L. S., K. S. McCallum, and L. Collier. Formation of Bis(chloromethyl) Ether from Formaldehyde and Hydrogen Chloride. Environ. Sci. Technol., 8(4):356-359, 1974.

(11) Kallow, G. J. and R. A. Solomon. Formation of Bis(chloromethyl) Ether in Simulated Hydrogen Chloride-Formaldehyde Atmospheric Environments. Amer. Ind. Hyg. Assoc. J., 34:469-473, November 1973.

CLASSIFICATION

CLASSIFICATION

TABLE 3. AMOUNT OF BCME FORMED AT VARIOUS RELATIVE HUMIDITIES AND ROOM TEMPERATURE AT VARIOUS CH_2O/HCl CONCENTRATIONS IN AIR (11)

CH_2O/HCl, ppm/ppm	BCME, ppb
3,000/10,000	48
750/10,000	2
1,000/500	0.6
500/1,000	0.3
500/1,000	0.3

humid air. The results of Tou (12) show the half-life of BCME to be as long as 25 hours in air. The results of their study of the hydrolysis of BCME in air in various reaction vessels are shown in Table 4. These results for the formation and hydrolysis of BCME in air have been included in this report because any BCME formed in air can enter the aquatic system through washout or absorption.

TABLE 4. HYDROLYSIS HALF-LIFE OF BCME IN HUMID AIR (12)

Reactor material	T, °C	Relative humidity, %	Half-life, hr
Glass	25	67	20
Fused ground glass	25	81	25
Fe_2O_3-powder	23	42	9.0
Coated saran	23	81	7.2

SIX TYPING LINES REMAIN

(12) Tou, J. C. and G. J. Kallos. Kinetic Study of the Stabilities of Chloromethyl Methyl Ether and Bis(chloromethyl) Ether in Humid Air. Anal. Chem., 46(12):1866-1869, 1974.

CLASSIFICATION

CLASSIFICATION

In aqueous systems typically, BCME is rapidly hydrolyzed as reported by Tou and associates (13-15). However, there is potential for the formation of BCME in fairly significant concentrations in acidic formalin solutions in contact with material containing chloride ions. The potential for the formation of BCME in such formalin solutions is discussed below followed by a review of the hydrolytic rates of BCME in more normal aqueous solutions.

Frankel, et al., (10) have monitored the vapors above formalin slurries of Friedel-Crafts chloride salts and detected BCME in concentrations from 210 ppb with $FeCl_3$ to 1,500 ppb with $AlCl_3$. Marceleno, et al., (16) also found BCME in solutions containing $MgCl_2$ catalysts. BCME was found to form in the chloromethylating medium (HCl-CH_2O-$ZnCl_2$) (17). These results indicate that fairly significant amounts of BCME could be present in any formalin solution which contains chloride ion. This result would present a problem in wastewater samples if high concentrations of formalin solution and chloride ion were present.

Recent publications by Tou and associates provide details of studies of the hydrolysis of BCME in aqueous media. In one study, hydrolysis rates were measured for a 1-ppm concentration of BCME in acidic, basic, and neutral aqueous solutions. Results

---

(13) Tou, J. C., L. B. Westover, and L. F. Sonnabend. Kinetic Study of Bis(chloromethyl) Ether Hydrolysis by Mass Spectrometry. J. Phys. Chem., 78(11):1096-1098, 1974.

(14) Tou, J. C. and G. J. Kallow. Study of Aqueous HCl and Formaldehyde Mixtures for Formation of Bis(chloromethyl) Ether. Amer. Ind. Hyg. Assoc. J., 35:419-422, July 1974.

(15) Tou, J. C., L. B. Westover, and L. F. Sonnabend. Analysis of a Non-Crosslinked, Water Soluble Anion Exhange REsin for the Possible Presence of Parts Per Billion Level of Bis(chloromethyl) Ether. Amer. Ind. Hyg. Assoc. J., 36:374-378, May 1975.

(16) Marceleno, T. and P. J. Bierbaum. A Preliminary Report on the Formation and Detection of Bis-Chloromethyl Ether in the Industrial and Medical Environment. Presented at American Industrial Hygiene Association Conference, Miami, Florida, 12-17 May 1974.

(17) Alvarez, M. and R. T. Rosen. Formation and Decomposition of Bis(chloromethyl) Ether in Aqueous Media. Int. J. Environ. Anal. Chem., 4:241-246, 1976.

CLASSIFICATION

CLASSIFICATION

of this study, presented in Table 5 (13), indicate that under the conditions listed BCME will not survive long enough to permit analysis using the techniques to be studied in this program.

TABLE 5. HYDROLYSIS OF BIS(CHLOROMETHYL) ETHER IN WATER AND AQUEOUS HCl AND NaOH (13)

	Half-life, s		
Solution	At 0°C	At 20°C	At 40°C
2N NaOH	88	29	11
1N NaOH	108	22	5
H_2O	277	38	7
1N HCl	365	38	6
2N HCl	630	63	8

A second study by Tou and associates showed that the hydrolysis rate of BCME is 14 seconds when equal concentrations of hydrochloric acid and formaldehyde (at 1, 10, 100, 250, and 1,000 ppm) are added to water (14). A third study by the same workers investigated whether the hydrolysis rate of BCME in water would be changed by the presence of a final product (a non-crosslinked, water-soluble, anion exchange resin) produced from BCME (15). Results of the study showed that no BCME existed in the product. In a spiked mixture of BCME with the resin and water, BCME was still hydrolyzed very rapidly. From these studies, it is apparent that the only possible way for BCME to remain in wastewater solution is in a very rapidly agitated water solution containing a non-water-soluble organic phase in which BCME has a favorable distribution coefficient compared to water. Even in this situation, BCME would be continually partitioning back into the aqueous phase due to the hydrolysis of the BCME fraction in the aqueous phase.

DETECTION OF HALOETHERS IN WATER

Since Rosen, et al., (18) discovered the presence of bis(2-chloroethyl) ether in the Kanawaha River in West Virginia in 1964, a number of other government workers have reported the detection of haloethers in industrial wastewater, river water, and drinking

SIX TYPING LINES REMAIN

(18) Rosen, A. A., R. T. Skeel, and M. B. Ettinger. Relationship of River Water Odor to Specific Organic Contaminants. J. Water Pollut. Contr. Fedr., 35(6):777-782, 1963.

CLASSIFICATION

water. Table 6 summarizes the compounds found, concentration if determined, and location; references are also provided (18-25).

METHODS FOR THE ISOLATION, CONCENTRATION, AND ANALYSIS OF HALOETHERS

The isolation, concentration, and analysis methods described in the literature have been directed primarily toward four of the haloethers (BCME, BCEE, BCIPE, and BCEXM) of interest in this program. The reported methods are described separately below for haloethers in air and in water. The air methods are included primarily to describe the gas chromatographic columns which have been utilized to date for the haloethers.

Haloethers in Air

The primary focus of methods for haloethers in air has been directed toward collection and analysis of BCME; few other references cover methods for other haloethers in air. Three main types of methods have been employed for collection and concentration of haloethers: direct analysis, absorbers, and derivatives. These three methods are discussed in the subsequent

---

(19) Frilous, J. Petrochemical Wastes as a Pollution Problem in the Lower Mississippi River. Paper submitted to Senate Subcommittee on Air and Water Pollution, 5 April 1971.

(20) Industrial Pollution of the Lower Mississippi River in Louisiana. PB 229 814, U.S. Environmental Protection Agency, Region VI, Dallas, Texas. April 1972. 154 pp.

(21) Kleopfer, R. D, and B. J. Fairless. Characterization of Organic Components in a Municipal Water Supply. Environ. Sci. Technol., 6(12):1036-1037, 1972.

(22) Analytical Report New Orleans Area Water Supply Study. EPA 909/9-75-003, 1975. 90 pp. U.S. Environmental Protection Agency, Region VI, Dallas, Texas.

(23) Webb, R. G., A. W. Garrison, L. H. Keith, and J. M. McGuire. Current Practice in GC-MS Analysis of Organics in Water. EPA-R-73-277, U.S. Environmental Protection Agency, Athens, Georgia, August 1973. 94 pp.

(24) Manwaring, J. F., W. M. Blankenship, L. Miller, and F. Voigt. Bis(chloroethyl) Ether in Drinking Water - Its Detection and Removal. J. Amer. Water Works Assoc., 69:210-213, April 1977.

(25) Dressman, R. C., J. Fair, and E. F. McFarreh. Determinative Method for Analysis of Aqueous Sample Extracts for Bis(2-Chloro)Ethers and Dichlorobenzenes. Environ. Sci. Technol., 11(7):719-721, 1977.

TABLE 6. HALOETHERS DETECTED IN WATER

Compounds	Concentration, µg/liter	Location	Reference
Bis(2-chloroethyl) ether	-[a]	Kanawha River, West Virginia	18
Bromophenyl phenyl ether	-[a]	New Orleans drinking water	19
Bromophenyl phenyl ether	-[a]	Jefferson Parish No. 2	20
Bis(2-chloroethyl) ether	-[a]	Jefferson Parish No. 2	20
Bis(2-chloroisopropyl) ether	-[a]	Jefferson Parish No. 2	20
Bis(2-chloroethyl) ether	-[a]	Evansville, Indiana drinking water	21
Bis(2-chloroisopropyl) ether	0.5 to 5.0	Evansville, Indiana	21
	2.0	Ohio River, Evansville	
Bis(2-chloroethyl) ether	0.07	Carrollton	22
	0.16	Jefferson Parish No. 1	22
	0.12	Jefferson Parish No. 2	22
Bish(2-chloroisopropyl) ether	0.18	Carrollton	22
	0.05	Jefferson Parish No. 1	22
	0.03	Jefferson Parish No. 2	22
Bis(2-chloroethoxy) methane	140,000	Synthetic rubber plant	23
Bis(2-chloroethyl) ether	160	Synthetic rubber plant	23
Bis(2-chloroisopropyl) ether	-[a]	Glycol plant thickening and sediment pond	23
Bis(2-chloroethyl) ether	10	Philadelphia Northeast water treatment plant	24
Bis(2-chloroethyl) ether	0.4	Delaware River, Philadelphia	24
Bis(2-chloroethyl) ether	0.01 to 0.36	Various cities during NOMS	25
Bis(2-chloroisopropyl) ether	0.02 to 0.55	Various cities during NOMS	25

[a]Detected but not quantified.

paragraphs; where appropriate, the gas chromatographic column and type of detector are described.

Direct Analysis--
A number of laboratory studies, primarily involving the formation or hydrolysis of BCME, have utilized the direct analysis of air and water samples (12-15). In these studies, a semi-membrane silicone fiber probe was used and connected directly to a high-resolution mass spectrometer.

Direct analysis for fumigant gases was performed by Berck (26) using a (1.8 m x 4 mm) stainless-steel column packed with 10% SE-30 on Diatoport S. The gases were analyzed for BCEE, and a thermal conductivity detector was used.

Absorbers--
A variety of absorbers have been used to collect haloethers (primarily BCME) from air. The absorbers were subsequently thermally desorbed onto a gas chromatographic column connected to a low- or high-resolution mass spectrometer. Table 7 cites the haloethers collected, the absorber used for collection, the gas chromatographic column employed, and the literature reference from which these data were taken (10, 11, 27-35).

---

(26) Berck, B. Determination of Fumigant Gases by Gas Chromatography. J. Agr. Food Chem., 113:373-377, 1965.

(27) Collier, L. Determination of Bischloromethyl Ether in the ppb Level in Air Samples by High Resolution Mass Spectroscopy. Environ. Sci. Technol., 6(10):930-932, 1972.

(28) Shadoff, L. A., G. J. Kallos, and J. S. Woods. Determination of Bis(chloromethyl) Ether in Air by Gas Chromatography - Mass Spectrometry. Analytical Chemistry, (45(14): 2341-2344, 1973.

(29) Ellgehausen, D. Determination of Volatile Toxic Substances in the Air by Means of a Coupled Gas Chromatograph - Mass Spectrometer System. Analytical Letters, 8(1):11-23, 1975.

(30) Sawicki, E. Bis(chloromethyl) Ether (Bis-CME) in Air Analytical Method. Health Lab Sci., 12:403-406, 1975.

(31) Pellizzari, E. D., B. H. Carpenter, J. E. Bunch, and E. Sawicki. Collection and Analysis of Trace Organic Pollutants in Ambient Atmospheres - Techniques for Evaluating Concentration of Vapors by Sorbent Media. Environ. Sci. Technol., 9(6):552-555, 1975.

(32) Pellizzari, E. D., B. H. Carpenter, and J. E. Bunch. Collection and Analysis of Trace Organic Vapor Pollutants in Ambient Atmospheres, Thermal Desorption of Organic Vapors

(Continued)

TABLE 7. ANALYSIS OF HALOETHERS IN AIR WITH POROUS POLYMER ABSORBER/GAS CHROMATOGRAPHY/MASS SPECTROMETRY

Haloether	Absorber	Gas chromatographic column	Reference
BCME	Porapak Q	-	27
BCME	Ascarite/ Chromosorb 101	Chromosorb 101	11
BCME	Chromosorb 101	Chromosorb 11 (1.22 m x 2 mm or 4 mm)	28
BCME	Porapak Q	OV-225	10
BCME	Porapak Q	3% OV-225 on Chromosorb W 80/100 mesh, 3 m x 2 mm	29
BCME	Chromosorb 101	-	30
BCME, BCEE	Chromosorb 101	2% DEGS on Chromosorb W	31
	Chromosorb 104 Tenax-GC Porapak Q Activated carbons 20% Carbowax 600 on Chromosorb W Carbowax 400/Porasil C Oxypropionitrile/ Porasil C 25% Didecylphthalate on Chromosorb P 20% Tricresyl phosphate on Chromosorb W	(HP) 80/100 mesh, 3.6 m x 2.5 mm	32
BCME	Porapak Q Tenax Chromosorb 101 Chromosorb 104	Porapak Q (1.8 m, 50/80 mesh) Chrosorb 101 (1.8 m, 80/100 mesh) 15% Polyterg B-300 on Chromosorb P (3.6 m, 60/80 mesh) 7% OV-225 on Gas Chrom Q (3.6 m, 80/100 mesh) 20% Carbowax 20M-TPA on Chromosorb W (4.6 m, 60/80 mesh) 10% DC-200 (3.1 m) 7% OV-225 (4.6 m) OF-1(1.95%)/OV-17(1.5%)(6.1 m) 1% SP-1000(6.1 mm)	33
BCME, BCEE	Tenax-GC	Tenax GC (3.6 m x 2.5 mm) 2% DEGS on Supelcoport (80/100 mesh)(3.6 m x 2.5 mm)	34
BCME	Porapak Q	30% Polyethylene glycol adipate on 100/120 mesh Celite (2.7 m x 4 mm)	35

CLASSIFICATION

Two methods based on the use of absorbers for collection utilize solvent for desorption. The National Institute of Occupational Safety and Health (NIOSH) traps BCEE from workplace environments on charcoal. The BCEE is desorbed with carbon disulfide and analyzed using gas chromatography on 10% FFAP on 80/100 mesh, acid-worked, DMCS-treated Chromosorb W (36).

An approach developed by MRC for the EPA's Office of Toxic Substances (37) under contract for the analysis of β-chloroethers (chloroethyl ethyl ether, CEVE, BCEE, BCIPE, BCEXM, and 1,2 bis[2-chloroethoxy] ethane) in air involves the use of Tenax-GC as an absorber. The Tenax-GC tube is then desorbed with methanol and analyzed using gas chromatography/mass spectrometry. The gas chromatographic colmn is Tenax-GC, and the mass spectrometer is operated in the selected-ion mode.

Derivative--
The third procedure used to collect and analyze BCME in air is based on derivative formation followed by gas chromatography with an electron capture detector. The derivatives are formed via the reaction in methanol solution between BCME being scrubbed from the air and the sodium salt of 2,4,6-trichlorophenol. Other sodium salts of alkyl or aryl oxides have been used by other

(Continued)

from Solid Media. Environ. Sci. Technol., 9(6)556-560, 1975.

(33) Frankel, L. S. and R. F. Black. Automatic Gas Chromatographic Monitor for the Determination of Parts-Per-Billion Levels of Bis(chloromethyl) Ether. Anal. Chem., 48(4): 732-737, 1976.

(34) Pellizzari, E. D., J. E. Bunch, R. E. Berkley, and J. McRae. Collection and Analysis of Trace Organic Vapor Pollutants in Ambient Atmospheres, The Performance of a Tenax-GC Cartridge Samples for Hazardous Vapors. Analytical Letters, 9(1):45-63, 1976.

(35) Evans, K. P., A. Mathias, N. Mellar, and R. Selvester. Detection and Estimation of Bis(chloromethyl) Ether in Air by Gas Chromatography - High Resolution Mass Spectrometry. Anal. Chem., 47(6):821-824, 1975.

(36) NIOSH Analytical Methods for Set V. NIOSH-SCP V, National Institute for Occupational Safety and Health, Cincinnati, Ohio, December 1976. 43 pp.

(37) Sherman, P. L., A. M. Kemmer, L. Metcalf, and H. D. Toy. Environmental Monitoring Near Industrial Sites: β-Chloroethers. EPA 56/6-78-003, U.S. Environmental Protection Agency, Washington, D.C., 1978. 271 pp.

CLASSIFICATION

CLASSIFICATION

workers. The materials used to form derivatives, the gas chromatographic colmn used for analysis, and the literature reference are listed in Table 8 (38-40).

TABLE 8. DERIVATIVE FORMATION FOR ANALYSIS OF BCME IN AIR

Derivative reagent	Gas chromatographic column	Reference
Sodium 2,4,6-trichlorophenate	0.1% QF-1 and 0.1% OV-17 on 100/200 mesh textured glass beads (GLC 100)(1.8 m x 4 mm)	38
Sodium phenate Sodium methoxide Sodium ethoxide Sodium thiophenate Sodium 2,4,6-trichlorophenate	LAC-2R446 + 2% H_3PO_4	39
Sodium 2,4,6-trichlorophenate	-	40

The major methods for the isolation and concentration of haloethers from water have centered around sorption on charcoal or solvent extraction. Methods of analysis are primarily gas chromatography with different detectors.

(38) Solomon, R. A. and G. J. Kallos. Determination of Chloromethyl Methyl Ether and Bis Chloromethyl Ether in Air at the Parts Per Billion Level by Gas-Liquid Chromatography. Anal. Chem., 47(6)955-957, 1975.

(39) Solomon, R. A. Detection of Chloromethyl Methyl Ether or Bischloromethyl Ether, U.S. Patent 3,944,389 (to Dow Chemical Co.), 16 March 1976.

(40) Sawicki, E. Analytical Method for Chloromethyl Methyl Ether (CMME) and Bischloromethyl Ether (BCME). Health Lab Sci., 13:78-81, 1976.

CLASSIFICATION

Table 9 lists the method of isolation and concentration, the gas chromatography detector, and the literature reference for haloethers in water (18, 21, 23, 41). In addition to these standard techniques, Deinzer, et al., tested the use of a cellulose acetate reverse-osmosis membrane for concentrating BCEE and BCIPE from water (42). They were not successful in increasing the concentration of these two compounds in the reject water using that specific membrane.

TABLE 9. ANALYSIS OF HALOETHERS IN WATER

Haloether	Isolation concentration technique	Gas chromatograph column	Detector	Reference
BCEE, BCIPE	Carbon chloroform extraction	-	IR	18
BCEE, BCIPE, BCEXM	Solvent	4% FFAP on Chromosorb W (1.8 m x 2.1 mm or 4 mm)	FID, mass spectrometry	23
BCEE, BCIPE	Carbon chloroform extraction	5% SE-30 on Chromosorb W 60/80 mesh (1.8 m x 2 mm)	FID, mass spectrometry	21
	Extraction with 5% ethyl ether in hexane	5% OV-17 on Chromosorb W 60/80 mesh (1.8 m x 2 mm)		
BCEE, BCIPE	Extraction with 15% ethyl ether in hexane	4% SE-30 + 6% OV-210 on Gas Chrom. Q (1.8 m x 2.1 mm)	Microcoulometric, electrolytic conductivity	25
		3% SP-1000 on Supelcoport 100/120 mesh (1.8 m x 2.1 mm)		
BCEM, CEVE	Purge and trap	0.2% Carbowax 1500 on Carbopak C (60/80 mesh) (2.4 m x 2.1 mm) + Carbowax 1500 on Chromosorb W (0.3 m x 2.1 mm)	Mass spectrometry	41
BCIPE, BCEE, BPPE	Methylene chloride extraction	1% SP-2250 on Supelcoport (100/120 mesh) (1.8 m x 2 mm)	Mass spectrometry	41
BCIPE, BCEE		OV-17 SCOT column	Mass spectrometry	41

(41) Sampling and Analysis Procedures for Screening of Industrial Effluents for Priority Pollutants, U.S. Environmental Protection Agency, Cincinnati, Ohio, April 1977.

(42) Deinzer, M., R. Melton, and D. Mitchell. Trace Organic Contaminants in Drinking Water; Their Concentration by Reverse Osmosis. Water Res., 9:799-805, 1975.

CLASSIFICATION

SECTION 4

GAS CHROMATOGRAPHY STUDIES

Gas chromatography studies were conducted to determine the optimum column and conditions for use with haloethers. In addition, electron capture and electrolytic conductivity detectors were studied to determine the most selective and sensitive detector for use with the haloethers. The results of these studies are described in the following subsections.

In summary, initial studies of the gas chromatography of the haloethers resulted in the selection of SP-1000 on Supelcoport over Tenax-GC as the column of choice. Early studies of detector sensitivity showed that the electron capture detector was more sensitive than the electrolytic conductivity detector. Unfortunately, bis(2-chloroisopropyl) ether was found to contain a large number of electron-capturing impurities, while showing no significant impurities with either the electrolytic conductivity detector or the flame ionization detector. Because of the BCIPE electron-capturing impurities, work was continued on the electrolytic conductivity detector and the resulting improvements made possible the use of this detector. With the modified electrolytic conductivity detector, sensitivity was approximately equal to electron capture and flame ionization detectors but with much greater specificity. The retention time was determined for bis(chloromethyl) ether on the SP-1000 column under the same conditions as those used for the other haloethers. Details regarding this work are provided below.

COLUMNS AND CONDITIONS

Previous work with similar compounds indicated two columns worthy of more detailed study. The columns were packed with SP-1000 on Supelcoport or with Tenax-GC. Both yielded adequate separations. Conditions found to be optimum for both columns are listed in Table 10. Figures 1 and 2 consist of the chromatograms obtained with SP-1000, and Figures 3 and 4 were obtained with Tenax-GC. Table 11 lists the retention time of the six haloethers on the two columns relative to Aldrin. The superior peak shapes for the haloethers when chromatographed on the column packed with SP-1000 make this the column of choice. An important fact learned during this study concerning SP-1000 was the need to use ultra-high-purity (UHP) grade helium as carrier gas. When regular-grade helium, nitrogen, or argon/methane (95/5) are used

CLASSIFICATION

TABLE 10. HALOETHER CHROMATOGRAPHIC CONDITIONS FOR COLUMNS PACKED WITH SP-1000 OR TENAX-GC

Item	Description/value
Chromatograph	Hewlett-Packard Model 5700
Injection port temperature	250°C
Column gas flow	40 mL/min helium
Column	1.8 m x 2.1 mm, glass packed with 3% SP-1000 on supelcoport (100/120 mesh) or Tenax-GC (60/80 mesh)
Column program	SP-1000 - 60°C for 2 min, programmed at 8°C/min to 230°C
	Tenax - 150°C for 4 min, programmed at 16°C/min to 310°C
Detector conditions for Figures 1 through 4	
Hall 700 furnace	850°C
Hall-electrolyte flow	3.0 mL/min, 40/60 isopropyl alcohol/ water
FID temperature	300°C
Gases	
Column effluent	40 mL/min helium split with 26 mL/min to Hall and 14 mL/min to FID
Hall	24 mL/min helium makeup; 50 mL/min hydrogen
FID	30 mL/min hydrogen; 240 mL/min air

Sample: 1 µL of hexane containing:

Compound	Concentration, ng/µL
CEVE	262
BCEE	305
BCIPE	275
BCEXM	300
CPPE	250
BPPE	355
Aldrin	275

TABLE 11. RETENTION TIMES OF HALOETHERS ON TWO GC COLUMNS RELATIVE TO ALDRIN

Compound	Column packed with SP-1000 on Supelcoport	Column packed with Tenax-GC
CEVE	0.12	0.25
BCEE	0.41	0.50
BCIPE	0.37	0.53
BCEXM	0.58	0.60
CPPE	0.86	0.81
BPPE	0.94	0.88
Aldrin	1.00	1.00

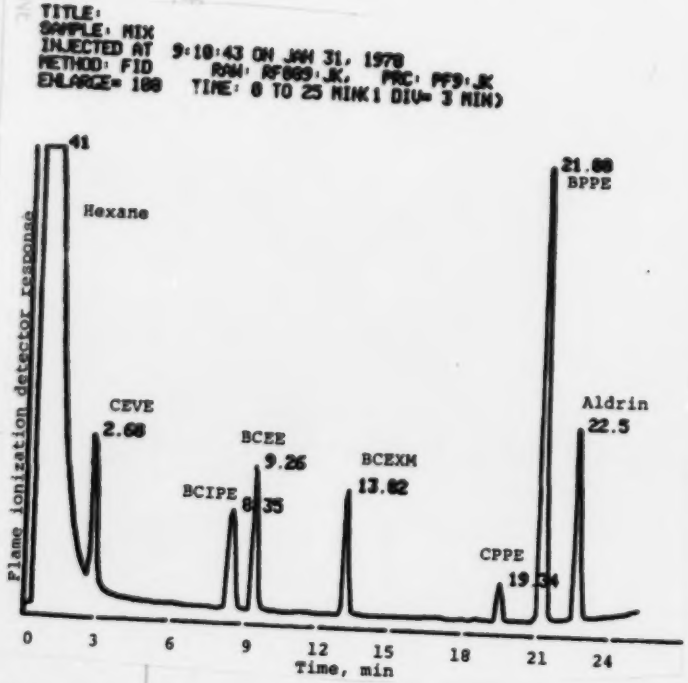

Figure 1. Chromatogram of haloethers on column packed with SP-1000 on Supelcoport and using flame ionization detector (see Table 10 for conditions).

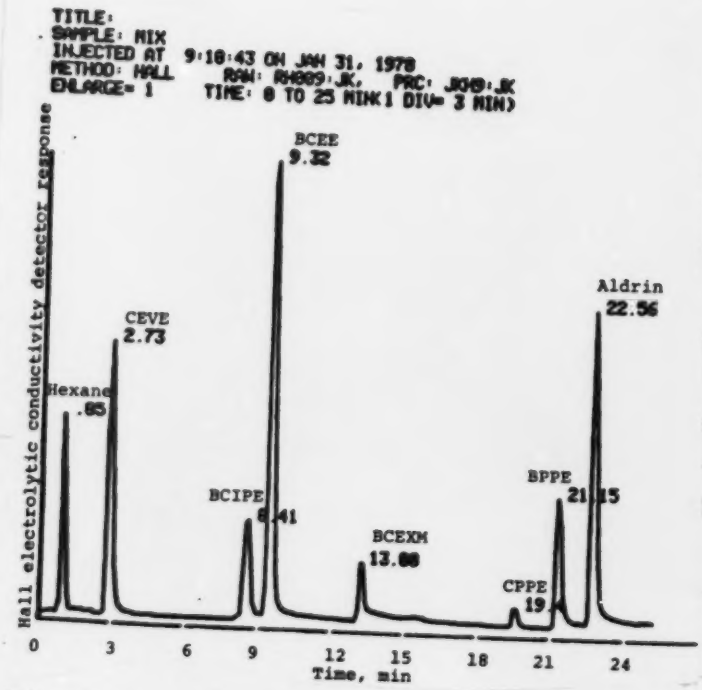

Figure 2. Chromatogram of haloethers on column packed with SP-1000 on Supelcoport and using Hall electrolytic conductivity detector (see Table 10 for conditions).

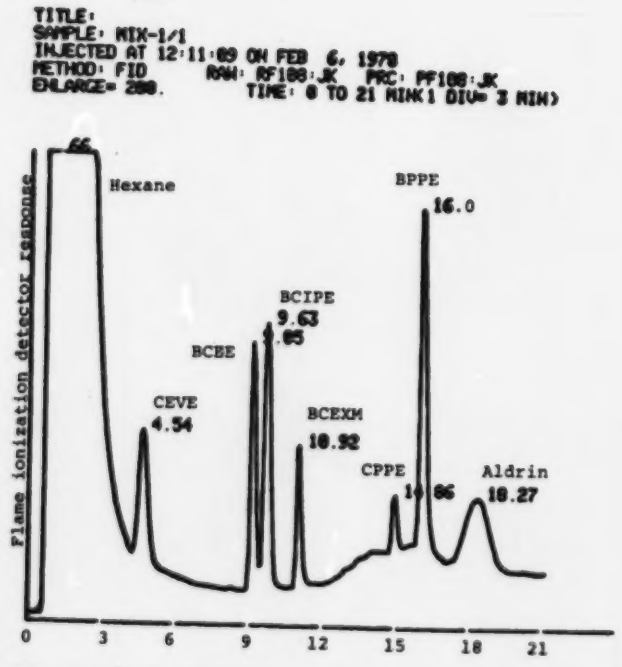

Figure 3. Chromatogram of haloethers on column packed with Tenax-GC and using flame ionization detector (see Table 11 for conditions).

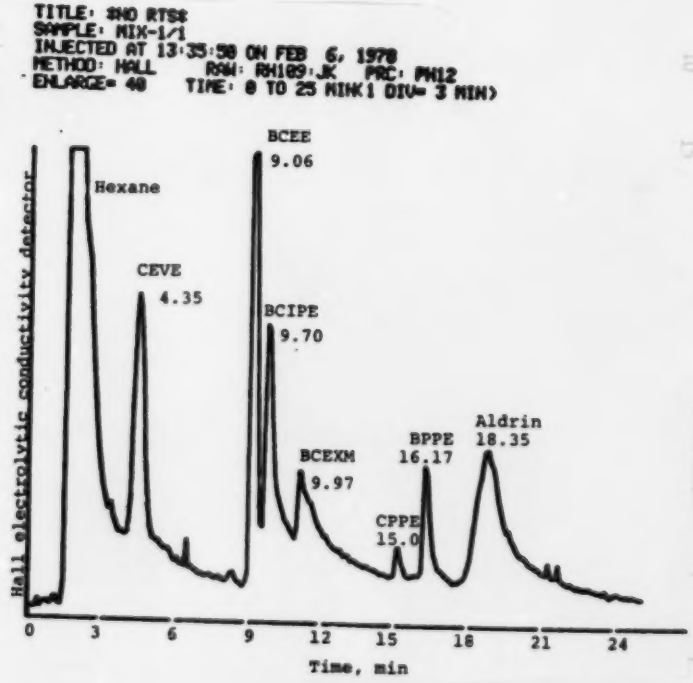

Figure 4. Chromatogram of haloethers on column packed with Tenax-GC and using Hall electrolytic conductivity detector (see Table 11 for conditions).

as carrier, the peak shape of the haloethers degrades with time. With the use of UHP-grade helium, no peak shape degradation was observed for the SP-1000 column when used continuously for thirty days.

After the initial column and conditions study was completed, additional work refined the chromatographic conditions using the SP-1000 column. The new conditions reduced the chromatographic run time from over 21 minutes to less than thirteen minutes. There was no sacrifice in peak separation in spite of a 40% savings in time. The new chromatographic conditions are listed in Table 12, with the resulting chromatogram in Figure 5.

TABLE 12. NEW HALOETHER CHROMATOGRAPHIC CONDITIONS FOR COLUMN PACKED WITH SP-1000

Item	Description/value
Chromatograph	Hewlett-Packard Model 5710 A
Injection port temperature	250°C
Auxiliary transfer line	250°C
Column gas flow	30 mL/min UHP-grade helium
Column	1.8 m x 2.1 mm, glass, packed with 3% SP-1000 on Supelcoport (100/120 mesh)
Column program	100°C for 4 min, programmed at 16°C/min to 230°C
Detector conditions for Figure 5	
Hall 310 furnace	850°C
Hall-electrolyte flow	0.5 mL/min, 50/50 ethyl alcohol/water
Hydrogen flow	70 mL/min

Sample: 1 µL of acetone containing:

Compound	Concentration, ng/µL
BCIPE	50
BCEE	62
BCEXM	53
CPPE	50
BPPE	52

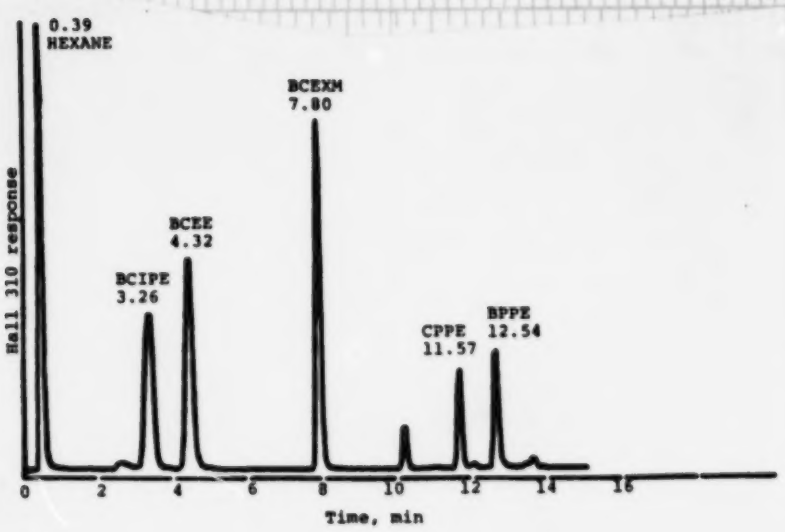

Figure 5. Chromatogram of haloethers with new conditions (see Table 12 for conditions).

INITIAL DETECTOR STUDIES

In the early stages of this study, the electron capture detector seemed to be the best candidate for final selection as the method for haloether detection. Linearity was very good for all compounds being studied. Figure 6 shows an example of this linearity for CPPE. Although the sensitivity and reproducibility data (see Tables 14 and 15 near the end of this section) are not impressive, it was felt that refinement in technique and conditions could improve results to the desired level. The greatest problem with the electron capture detector was created by one of the haloethers. Even the "purest" sample of BCIPE that we could obtain contained over 20 electron-capturing impurities. These impurities created peaks which interfered with other haloethers. Based on the desire to keep BCIPE in the study, it was decided to investigate other detectors. Data and sample chromatograms from these early studies are shown in Table 13 and Figures 7 and 8.

The flame ionization detector (FID) was used routinely during the selection of optimum conditions and columns. This detector gave very good results in sensitivity, linearity and reproducibility for our pure haloether standards (see Tables 14 and 15). However, knowing wastewaters contain many compounds which would be extracted and detected along with the haloethers, we did not consider the FID as our final detector choice because it is so non-specific.

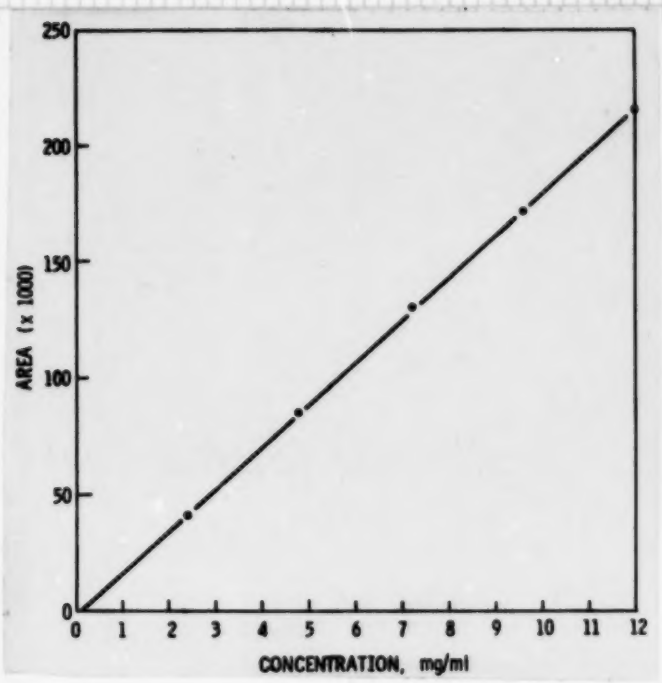

Figure 6. Calibration curve for CPPE.

TABLE 13. HALOETHER CHROMATOGRAPHIC CONDITIONS FOR COLUMN PACKED WITH SP-1000 AND USING ELECTRON CAPTURE DETECTOR

Item	Description/value
Chromatograph	Hewlett-Packard Model 5713
Injection port temperature	250°C
Electron capture detector temperature	300°C
Column	1.8 m x 2.1 mm, glass packed with 3% SP-1000 on supelcoport (100/120 mesh)
Column program	60°C for 2 min, then programmed at 8°C/min to 230°C
Gases	
Column	40 mL/min ultra-high-purity helium
Electron capture makeup	20 mL/min, 5% methane in argon

Sample: 2 µL of hexane containing:

Ether	Concentration, ng/µL
CEVE	205
BCEE	138
BCEXM	133
CPPE	50
BPPE	8

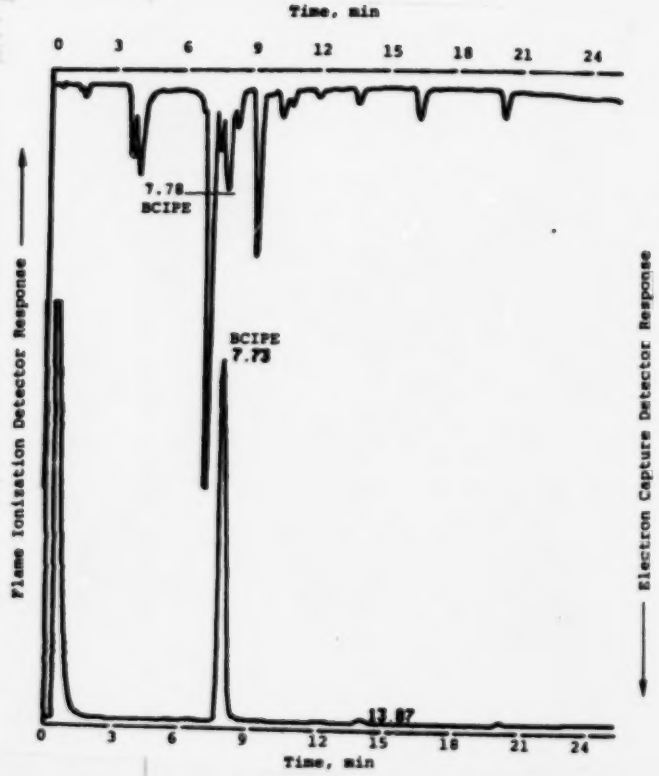

Figure 7. Chromatogram of BCIPE on column packed with SP-1000 and detected simultaneously using FID and electron capture detectors, showing electron-capture impurities.

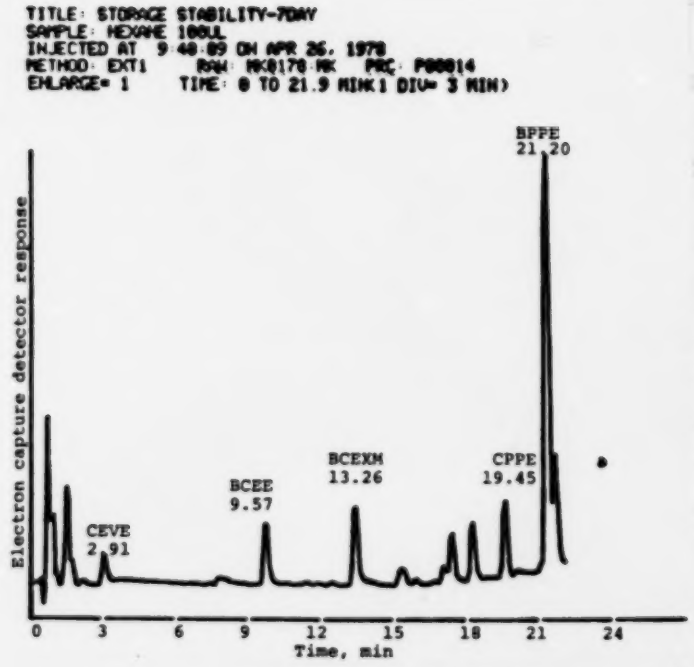

Figure 8. Chromatogram of haloethers on column packed with SP-1000 and detected using an electron capture detector.

The early work with the model 700 Hall electrolytic conductivity detector was not very promising. If this detector were to be used, sensitivity and reproducibility would have to be improved (see Tables 14 and 15). It was difficult to stabilize the unit each day, and linearity of results over a wide range of concentrations was not possible. In spite of these problems, it was decided to be worthwhile to develop the system because of the Hall's specificity.

A number of changes were made on the model 700 Hall detector which significantly improved the sensitivity and the reproducibility of the detector (see Tables 14 and 15). The major changes were:

- The addition of a glass-lined, heated (∿275°C) collection port at the exit of the chromatograph as well as the heating of the transfer line.
- The use of ethanol/water or absolute ethanol as the electrolyte solution instead of isopropanol/water.
- Modifications on the exit end of the quartz tube, such as the use of Teflon instead of stainless steel and the insertion of the tube from the detector cell up into the end of the quartz tube.

The Hall detector still does not give linear results over a wide range of concentrations, but careful calibration will give reliable values for the haloethers. The greatest advantage of this system is the specificity for the compounds of this study. Figure 9 shows a sample chromatogram from the modified model 700 Hall detector.

TABLE 14. SENSITIVITY FOR HALOTHERS

	5 x noise, ng			
Haloether	Electron capture	FID	Hall 700	Modified Hall 700
CEVE	40	1.5	8.4	0.5
BCIPE	9.0	0.65	46	0.45
BCEE	28	1.25	8.6	0.25
BCEXM	26	1.75	240	0.20
CPPE	12	0.25	5.8	1.1
BPPE	1.6	0.15	28	0.55

TABLE 15. REPRODUCIBILITY DATA

Standard manual injection - 1 µL solution containing:

CEVE	105 ng
BCIPE	100 ng
BCEE	98 ng
BCEXM	96 ng
CPPE	100 ng
BPPE	99 ng

	Relative standard deviation, percent				
Haloether	Electron capture	FID	Hall 700	Modified Hall 700	Hall 310
CEVE	10.4	42.5[a]	23.1	6.4	1.9
BCIPE	6.3	1.2	11.2	4.5	2.4
BCEE	11.1	1.2	22.1	3.4	4.6
BCEXM	15.5	0.8	37.7	3.7	2.4
BPPE	7.0	1.2	28.7	3.9	1.3

[a]Caused by the venting of the solvent peak.

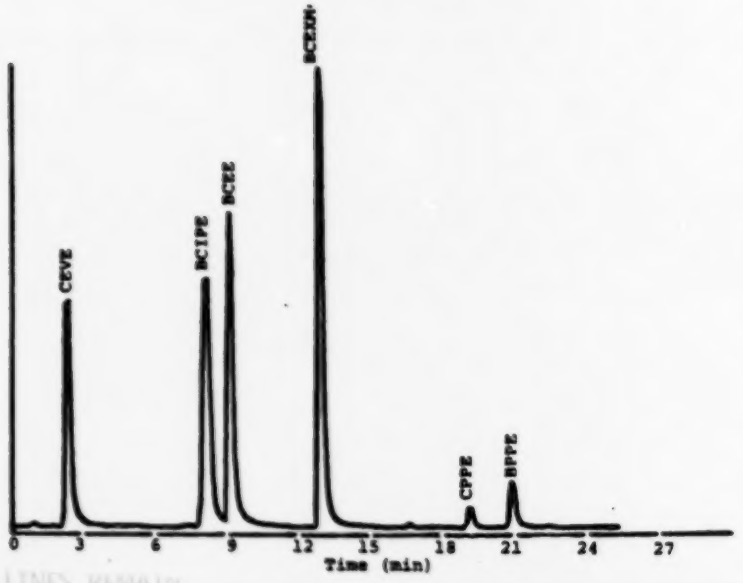

Figure 9. Chromatogram of haloethers on the modified Hall Model 700 detector.

The final detector used was the model 310 Hall electrolytic conductivity detector. As with the model 700 Hall, many alterations were needed before good results were possible. Results from the model 310 are comparable to those from the modified model 700 (see chromatogram in Figure 5).

Detector Summary and Recommendation

Each of the detectors discussed in this section has its own limitations; EC - interference peaks from BCIPE, FID - nonspecific, both Hall models - nonlinear over a wide range. The final selection of a detector must be based on the quality of results needed and the type of sample being analyzed. We have no control over the number or types of compounds in the wastewaters to be analyzed. Therefore, we feel it is essential to select a detector that is as specific as possible for our compounds. The Hall detector models are the most specific detectors discussed. The Hall's major problem (nonlinearity over wide ranges) can be overcome with careful calibration techniques, while the problems of the other detectors have no obvious solutions. We feel the electrolytic conductivity detector is the best choice for haloether detection.

Bis(chloromethyl) Ether

Bis(chloromethyl) ether was analyzed by gas chromatography using a column containing 3% SP-1000 on Supelcoport (100/120 mesh). The BCME elutes at approximately 2.7 minutes under the conditions normally employed for the haloethers (60°C for 2 minutes, then programmed at 8°C/min to 230°C and held at that temperature for 8 minutes). There was no problem in separating the BCME from the CEVE, as shown in Figure 10.

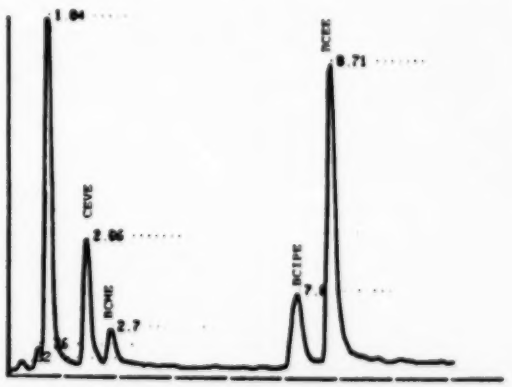

Figure 10. Chromatogram showing the response of BCME in comparison to three other haloethers on column packed with SP-1000 on Supelcoport.

SECTION 5

EXTRACTION STUDIES

Extraction studies for the six haloethers using spiked laboratory samples were conducted at three pH's (2, 7, and 10) with three solvents (methylene chloride, 15% ethyl ether in hexane, and pentane). Due to problems caused by the presence of a large number of electron-capturing impurities in BCIPE, it was necessary to perform a separate extraction study for the compound. The procedures used for the studies are described in detail for the pH 2 studies. The pH 7 and pH 10 extractions were conducted in exactly the same manner except for the composition of the buffers, which are described below.

Extraction at pH 2

Three one-liter buffered deionized water solutions were spiked with 10 µL of a standard solution of five of the haloethers (CEVE, BCEE, BCEXM, CPPE, and BPPE) in acetone. The deionized water was prepared by adding 0.82 mL of concentrated hydrochloric acid to one liter of water (0.01M). The concentrations of the five haloethers in the acetone spiking solution were 8.2 mg/mL of CEVE, 5.5 mg/mL of BCEE, 5.3 mg/mL of BCEXM, 0.32 mg/mL of BPPE, and and 2.0 mg/mL of CPPE. Three additional one-liter solutions of deionized water were spiked with 100 µL of an acetone solution containing 9.24 mg/mL of BCIPE.

The solutions were extracted immediately after spiking with three 60-mL portions of pentane. These extracts were combined and passed through a 2-gram bed of sodium sulfate which was held in a glass funnel by glass wool. The dried extracts were then evaporated using Kuderna-Danish evaporators to a volume of ∿4 mL. These concentrates were then transferred to tared, Viton, septum-capped vials and reweighed. The final volume of the concentrates was determined by dividing the net weight of the concentrates by the density of pentane.

The three extraction concentrates from the solutions spiked with the five haloethers (CEVE, BCEE, BCEXM, CPPE, and BPPE) were analyzed on a 1.8 m x 2.1 mm glass column packed with 3% SP-1000 on (100/200 mesh) Supelcoport, with an electron capture detector. The three remaining concentrates from solutions spiked with BCIPE were analyzed on a 1.8 m x 2.1 mm glass column packed with

(60/80 mesh) Tenax-GC, with a flame ionization detector. In both analyses, the areas of the peaks were integrated and the percent recovery determined by comparing the areas of the concentrates with those of standard samples. Calibration curves were determined for all six haloethers with the appropriate detector, and the curves were found to be linear in the concentration range used.

The extraction study was repeated for two other solvents (15% ethyl ether in hexane, and methylene chloride) using the same procedure as that described above for pentane. However, for these other solvents, the hexane was solvent exchanged for methylene chloride during the Kuderna-Danish evaporation. This solvent exchange was acomplished by allowing the methylene chloride to evaporate to ~6 mL, adding 20 mL of hexane and evaporating to 6 mL, and finally adding 10 mL of hexane and allowing the solvent to evaporate to ~4 mL.

Extraction at pH 7

Extraction studies at pH 7 were performed in the same manner as those studies at pH 2 except for the buffered deionized water. The buffered deionized water for the pH 7 studies was prepared by mixing 500 mL of 0.1M potassium dihydrogen phosphate with 291 mL of 0.1M sodium hydroxide and diluting to one liter.

Extraction at pH 10

Extraction studies at pH 10 were also performed in the same manner as those at pH 2 and pH 7 except for the buffered deionized water composition. The buffered solutions for the pH 10 studies were prepared by mixing 500 mL of 0.025M borax (sodium tetraborate) with 183 mL of 0.1M sodium hydroxide and diluting to one liter.

Results

The analytical results of the extraction studies are presented in Table 16. Each value listed for "percent recovered" represents an average of three different extractions at a given pH and for a given solvent. These results were analyzed using analysis of variance (ANOVA), and the resulting F values for each haloether and the average are listed in Table 17. For CEVE, pH was the only variable which contributed significantly to the total variance. For BCIPE, both pH and solvent were significant contributors to the variance. For the four other haloethers, only the solvent contributed to the variance. These ANOVA results, together with the data presented in Table 16, indicate that the best average recoveries of the haloethers are achieved using methylene chloride as solvent.

TABLE 16. RESULTS OF EXTRACTION STUDIES

pH	Haloether	Solvent: 15% Ethyl ether in hexane — Percent recovered (average)	15% Ethyl ether in hexane — RSD,[a] %	Methylene chloride — Percent recovered (average)	Methylene chloride — RSD,[a] %	Pentane — Percent recovered (average)	Pentane — RSD,[a] %
2	CEVE	29.6	32.4	31.3	9.5	37.8	32.1
	BCIPE	66.4	21.8	51.2	21.5	22.1[b]	--
	BCEE	66.9	16.3	69.7	20.3	43.4	9.8
	BCEXM	55.9	15.0	83.2	11.2	50.5	13.9
	CPPE	67.3	9.8	82.9	12.7	62.8	20.0
	BPPE	57.4	8.7	68.9	14.6	55.8	21.3
7	CEVE	65.9	16.5	70.7	31.5	61.7	47.3
	BCIPE	88.5	7.6	61.6	8.2	76.2	10.7
	BCEE	63.7	3.1	93.2	1.6	46.1	8.7
	BCEXM	68.0	14.5	88.0	7.3	43.3	27.8
	CPPE	65.1	12.5	85.6	6.8	61.1	12.5
	BPPE	57.1	12.7	81.3	6.3	63.1	6.5
10	CEVE	44.2	29.8	55.0	41.2	30.7	13.8
	BCIPE	61.7[c]	--	92.1	5.2	63.0	10.8
	BCEE	59.9	20.8	101.6	8.1	42.7	5.3
	BCEXM	54.5	24.7	75.3	8.5	38.4	6.4
	CPPE	54.4	30.8	93.2	4.3	66.1	2.3
	BPPE	52.7	30.4	82.9	1.9	67.3	0.56

[a]RSD = relative standard deviation.

[b]Value for one extraction.

[c]Average of two extractions.

TABLE 17. RESULTS OF ANOVA FOR SOLVENT EXTRACTION STUDIES

Variable	Degrees of freedom	T values	F values: CEVE	BCEE	BCEXM	CPPE	BPPE	BCIPE	Average
Solvent	2	3.55	0.69	72.05	34.8	20.65	16.6	18.1	27.1
pH	2	3.55	9.64	3.10	2.68	0.01	1.97	10.1	4.6
Replicates	2	3.55	1.22	1.49	1.11	0.005	0.61	0.73	0.86

CLASSIFICATION

The average recoveries for all six haloethers combined using methylene chloride as a solvent were 64.5%, 81.0%, and 83.4% at pH 2, pH 7, and pH 10, respectively. A t-test was employed to determine whether these means are statistically different from each other at the 95% confidence interval. The t-test indicated that there is a statistically significant difference in the mean values obtained at pH 2 and pH 7, and also at pH 2 and pH 10. There is, however, no difference in the mean values obtained at pH 7 and pH 10.

These statistical analyses indicate that when the six ethers are extracted by a group, the average variance due to the solvent used, the pH, and the reproducibility constituted approximately 60%, 10%, and 1%, respectively, of the total variance.

Chloroethyl Vinyl Ether

Because of the general inability to recover CEVE from the samples due to its volatility, it was decided to test CEVE for percent recovery as a purgeable. Hence, 50 µL of a solution containing 1.2 mg/mL of CEVE was injected into 5 mL of organic-free water. The sample was then sparged for 12 minutes with helium at a flow of 40 mL/min. The trapping device was a stainless-steel tube (0.3 m long, 3.2 mm OD) packed with ∿0.2 m of Tenax-GC and ∿50 mm of silica gel. After sparging, the tube was thermally desorbed onto a Carbowax column held at -40°C. The sample was then analyzed by GC/MS using a Hewlett-Packard 5981 GC/MS with a H-P 5934 data system. The conditions for the GC/MS analysis are listed in Table 18. The data for the percent recovery of CEVE by this method are listed in Table 19. A typical chromatogram is shown in Figure 11.

TABLE 18. CONDITIONS FOR GC/MS ANALYSIS OF CEVE

Item	Value/description
Carrier gas	Helium at 30 ml/min
Temperature program	-40°C to 180°C/min
Column and packing	1.8 m x 3.2 mm, stainless steel, packed with Carbowax 1500 on Carbopak C; 0.3 m x 3.2 mm, stainless steel, precolumn packed with Carbowax 1500 on Supelcoport
Injection port temperature	250°C

CLASSIFICATION

CLASSIFICATION

TABLE 19. PERCENT RECOVERY FOR CEVE

Major masses	Area average, three runs	Std. dev.	Rel. std. dev., %	Std. area	Recovery, %
63	41906	6592	15.7	12072	34.7
106	23974	2980	12.4	7889	30.4

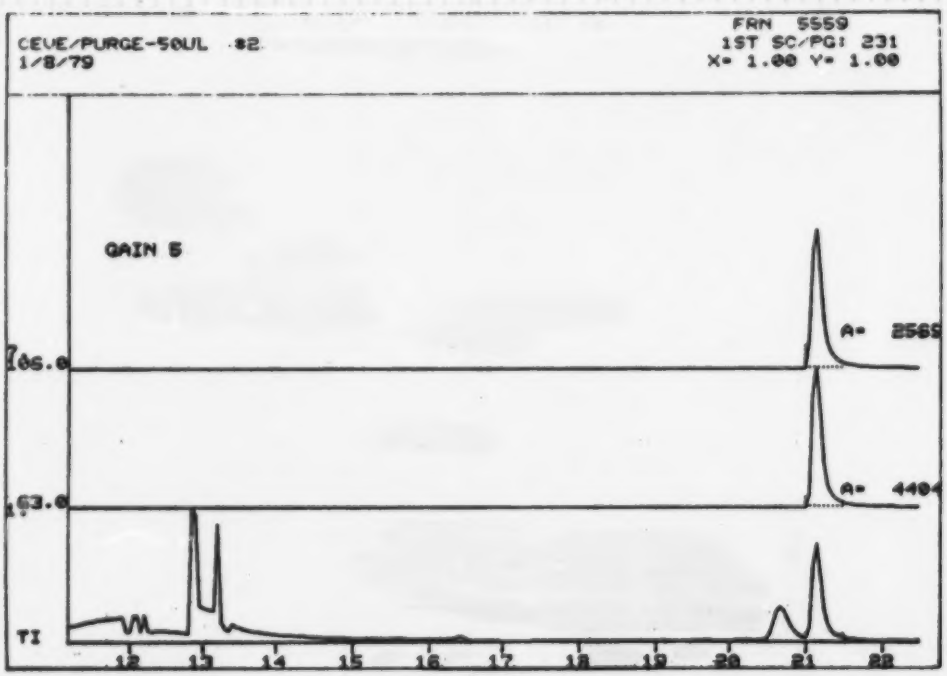

Figure 11. Typical chromatogram for CEVE with purge and trap system.

CLASSIFICATION

SECTION 6

PRESERVATION STUDIES

Preservation studies were conducted by spiking one-liter solutions of buffered deionized water at pH 2, pH 7, and pH 10 with the standard solution of five haloethers (CEVE, BCEE, BCEXM, CPPE, and BPPE) in acetone. The studies were conducted at residual chlorine levels of 0 ppm and 2 ppm and storage temperatures of 4°C and 25°C; storage time was seven days. Extraction of the stored solutions was performed using methylene chloride. In the following two sections, the composition of each sample is described and results are provided for the preservation study. The analytical portion of this study was done using the electron capture detector, therefore BCIPE was excluded because of the number of electron-capturing impurities.

Preparation

The preservation samples containing 0 ppm residual chlorine were prepared in the same manner as described in the extraction studies (Section 5). Once prepared, each solution was stored in a separate amber glass jug at 4°C or 25°C. Three sample solutions were stored at each set of conditions. The matrix of samples containing 2 ppm of residual chlorine were also prepared in the same manner except that 10 mL of a 432 mg/liter solution of calcium hypochlorite was added to each solution before dilution to one liter. This hypochlorite concentration generates a residual chlorine level of 2 ppm. After preparation, these solutions were stored in amber glass jugs as described above.

After storage, the solutions were extracted with methylene chloride. The methylene chloride extracts were combined, dried with sodium sulfate, concentrated, solvent exchanged with hexane, and analyzed as described for the extraction studies.

Results

The analytical results of the preservation studies are presented in Table 20. The "average percent recovered" values listed represent an average of three separate extractions.

These data were subjected to ANOVA testing and the results are shown in Table 21. These results are expressed in gross terms with "+" denoting significant contributions of the variable to

the variance and "-" showing no significant contribution. The effect of the pH-chlorine level interaction is as important as the main factors, chlorine level and pH. Temperature had no statistical effect on the variability. The pH-temperature interaction was significant for BCEE and BPPE.

TABLE 20. PRESERVATION STUDY RESULTS

pH	Chlorine, ppm	Haloether	At 4°C		At 25°C	
			Percent recovered (average)	RSD,[a] %	Percent recovered (average)	RSD,[a] %
2	0	CEVE	*	*	*	*
		BCEE	61.7	23.2	76.6	2.6
		BCEXM	75.7	22.0	71.0	3.5
		CPPE	78.7	9.5	86.9	3.8
		BPPE	90.6	7.6	91.9	4.6
2	2	CEVE	10.4	32.3	12.5	20.4
		BCEE	78.3	6.9	66.0	12.4
		BCEXM	66.2	22.3	89.0	9.7
		CPPE	20.2	60.5	16.4	61.0
		BPPE	18.7	70.2	11.5	25.2
7	0	CEVE	25.3	31.1	28.7	25.3
		BCEE	66.9	13.0	61.4	8.1
		BCEXM	65.3	24.0	71.4	5.7
		CPPE	80.3	10.3	74.0	8.0
		BPPE	87.9	8.8	76.5	2.6
7	2	CEVE	*	*	*	*
		BCEE	59.4	26.5	68.7	17.5
		BCEXM	68.1	10.1	54.9	20.8
		CPPE	73.2	5.4	70.3	7.6
		BPPE	79.3	9.8	72.5	6.6
10	0	CEVE	37.7	17.8	26.8	19.3
		BCEE	69.8	26.0	53.4	10.1
		BCEXM	63.8	26.0	54.0	20.3
		CPPE	66.6	22.3	63.3	1.5
		BPPE	78.4	18.2	57.3	8.0
10	2	CEVE	74.6	10.5	68.6	13.7
		BCEE	55.5	15.7	80.2	6.5
		BCEXM	78.8	4.0	70.2	16.9
		CPPE	68.2	8.2	76.9	9.2
		BPPE	60.8	42.0	77.1	0.76

[a]RSD = relative standard deviation.

* = none detected.

TABLE 21. RESULTS OF ANOVA ANALYSIS OF PRESERVATION STUDY RESULTS

Compound	Variable: Temperature	Cl_2 level	pH	pH-Cl_2 level	Temperature-pH
CEVE	-	+	+	+	-
BCEE	-	-	-	-	+
BCEXM	-	-	-	-	-
CPPE	-	+	+	+	-
BPPE	-	+	+	+	+

+ = Caused significant variation.
- = Caused no significant variation.

The data in Tables 20 and 21 show that the only precaution needed for sample preservation is an adjustment of the pH to at least 7 because of the sensitivity of CEVE to acid hydrolysis and the reaction between residual chlorine and BPPE and CPPE at acid pH. Closer examination of Table 20 shows that there is very little difference, if any, between preservation at pH 7 or pH 10. Also, the table shows little difference between preservation at 4°C or 25°C. Since preserving samples in ice for shipping is more time consuming, more expensive, and requires more care; it is fortunate that cold storage is not needed.

The data for CEVE appears to be most erratic. Much of this variance can be attributed to the extreme volatility of this compound. Recovery of the haloethers increases significantly with the removal of CEVE from the list as shown in Table 22.

TABLE 22. AVERAGE RECOVERY (%) OF HALOETHERS FROM PRESERVATION STUDY SAMPLES AT NEUTRAL AND BASIC pH

pH	Chlorine level, ppm	At 4°C: Five haloethers	At 4°C: Four haloethers	At 25°C: Five haloethers	At 25°C: Four haloethers
7	0	65.2	75.1	62.4	70.8
7	2	56.0	70.0	54.6	66.6
10	0	63.3	69.6	51.0	57.0
10	2	67.6	65.8	74.6	76.1

SECTION 7

SOLVENT STABILITY STUDIES

Five haloethers were included in the solvent stability study: CEVE, BCIPE, BCEE, BCEXM, and BPPE. CPPE was not included in this study because of its cost ($2/mg or $1,250 for the study). The concentrations used in this study were determined using the data generated in the sensitivity studies for the two detectors (electron capture and electrolytic conductivity). The concentrations used were equal to 1,000 times the baseline noise for the least sensitive detector. The concentration of the BCEXM was changed to 12.0 mg/mL because sufficient material was not on hand to use the concentration of 48.0 mg/mL in each solvent.

Acetone and methanol were the two water-miscible solvents used in this study. These materials were high-purity, "distilled in glass" solvents purchased from Burdick and Jackson. Each solution was made up in a 250-mL glass volumetric flask. Using a 5-mL syringe with 0.05-mL gradations, the compounds were added in the amounts shown in Table 23. Twelve 4-mL aliquots of each solution were quantitatively transferred, using a 4-mL glass pipet, into 5-mL prescored sealable-glass ampules. The ampules were placed in dry ice for cooling and then flame sealed. Immediately after sealing and after storage times of 30, 60, and 90 days, three ampules were opened, placed in septum-capped vials, and analyzed against fresh standards (Table 24) by gas chromatographic conditions are listed in Table 25. Data from the analyses of the solutions are shown in Tables 26 - 33; data from all four storage times are summarized in Table 34.

TABLE 23. CONCENTRATIONS OF SOLVENT SOLUTIONS (250 mL)

Compound	Amount added, mL	Concentration, mg/mL
CEVE	1.95	8.2
BCIPE	2.10	9.2
BCEE	1.15	5.6
BCEXM	2.50	12.0
BPPE	1.0	5.7

TABLE 24. CONCENTRATIONS OF STANDARDS (1 mL)

Compound	Amount added, µL	Concentration, mg/mL
CEVE	7.8	8.2
BCIPE	8.4	9.2
BCEE	4.2	5.6
BCEXM	8.6	10.3
CPPE	4.0	5.7

TABLE 25. HALOETHER CHROMATOGRAPHIC CONDITIONS WITH ELECTRON CAPTURE DETECTOR

Item	Description/value
Chromatograph	Hewlett-Parkard Model 5713
Injection port temperature	250°C
Electron capture detector temperature	300°C
Column	1.8 m x 2.1 mm, glass, packed with 3% SP-1000 on Supelcoport (100/120 mesh)
Column program	60°C for 2 min, then programmed at 8°C/min to 230°C
Gases	
Column:	40 mL/min ultra-high-purity helium
Electron capture makeup:	20 mL/min, 5% methane in argon

TABLE 26. CONCENTRATION OF INITIAL METHANOL SOLUTION USED FOR SOLVENT STABILITY STUDY

Haloether	Concentration added, µg/mL	Concentration found (avg. of 3 runs), µg/mL	Avg. rel. std. dev., %
CEVE	8.2		
BCIPE	9.2	9.2	5.1
BCEE	5.6	5.7	4.4
BCEXM	12	14	4.7
BPPE	5.7	5.4	0.91

TABLE 27. CONCENTRATION OF INITIAL ACETONE SOLUTION USED FOR SOLVENT STABILITY STUDY

Haloether	Concentration added, µg/mL	Concentration found (avg. of 3 runs), µg/mL	Avg. rel. std. dev., %
CEVE	8.2	9.9	4.9
BCIPE	9.2	9.9	2.4
BCEE	5.6	6.0	3.4
BCEXM	12	16	3.8
BPPE	5.7	5.4	0.48

TABLE 28. RESULTS OF ANALYSIS OF METHANOL SOLUTION AFTER STORAGE FOR 30 DAYS

Sample number	Haloether	Concentration (avg. of 3 runs), µg/mL	Avg. rel. std. dev., %	Percent change
30 M-1	CEVE	0	_[a]	_[a]
	BCIPE	9.6	8.0	+4.3
	BCEE	5.6	3.4	-1.8
	BCEXM	14	2.9	0.0
	BPPE	6.3	14	+17
30 M-2	CEVE	0	_[a]	_[a]
	BCIPE	9.6	7.2	+4.3
	BCEE	5.6	1.6	-1.8
	BCEXM	14	1.4	0.0
	BPPE	5.7	9.2	+6.0
30 M-3	CEVE	0	_[a]	_[a]
	BCIPE	9.8	4.6	+6.5
	BCEE	5.6	1.9	-1.8
	BCEXM	15	1.9	+7.1
	BPPE	5.9	14	+9.3

[a]Not determined.

TABLE 29. RESULTS OF ANALYSIS OF ACETONE SOLUTION AFTER STORAGE FOR 30 DAYS

Sample number	Haloether	Concentration (avg. of 3 runs), µg/mL	Avg. rel. std. dev., %	Percent change
30 A-1	CEVE	11	2.5	+11.1
	BCIPE	9.7	2.4	-2.1
	BCEE	6.0	3.7	0.0
	BCEXM	16	2.0	0.0
	BPPE	6.1	12	+13
30 A-2	CEVE	10.1	3.7	+2.0
	BCIPE	9.9	0.92	0.0
	BCEE	6.0	0.3	0.0
	BCEXM	16	1.0	0.0
	BPPE	6.3	13	+17
30 A-3	CEVE	10	3.8	+1.0
	BCIPE	10	1.1	+1.0
	BCEE	6.1	1.8	+1.7
	BCEXM	16	1.7	0.0
	BPPE	5.9	14	+9.3

TABLE 30. RESULTS OF ANALYSIS OF METHANOL SOLUTION AFTER STORAGE FOR 60 DAYS

Sample number	Haloether	Concentration (avg. of 3 runs), µg/mL	Avg. rel. std. dev., %	Percent change
60 M-1	CEVE	0	_[a]	_[a]
	BCIPE	9.0	3.2	-2.2
	BCEE	5.5	4.8	-3.6
	BCEXM	14	4.0	0.0
	BPPE	5.2	0.4	-3.8
60 M-2	CEVE	0	_[a]	_[a]
	BCIPE	9.1	1.2	-1.1
	BCEE	5.4	1.2	-5.6
	BCEXM	14	1.4	0.0
	BPPE	5.2	1.3	-3.8
60 M-3	CEVE	0	_[a]	_[a]
	BCIPE	9.3	2.9	+1.1
	BCEE	5.5	2.9	-3.6
	BCEXM	15	2.6	+6.6
	BPPE	5.2	11	-3.8

[a]Not determined.

TABLE 31. RESULTS OF ANALYSIS OF ACETONE SOLUTION AFTER STORAGE FOR 60 DAYS

Sample number	Haloether	Concentration (avg. of 3 runs), µg/mL	Avg. rel. std. dev., %	Percent change
60 A-1	CEVE	11	3.0	+10
	BCIPE	11	0.5	+10
	BCEE	6.3	0.9	+4.8
	BCEXM	17	0.7	+5.9
	BPPE	4.7	0.6	-15
60 A-2	CEVE	11	5.9	+10
	BCIPE	10	4.8	+10
	BCEE	6.2	5.4	+3.3
	BCEXM	17	7.7	+5.9
	BPPE	5.0	9.7	-8.0
60 A-3	CEVE	9.9	1.8	0.0
	BCIPE	9.5	1.6	-4.2
	BCEE	5.7	1.6	-5.2
	BCEXM	15	1.6	-6.7
	BPPE	4.4	0.5	-23

TABLE 32. RESULTS OF ANALYSIS OF METHANOL SOLUTION AFTER STORAGE FOR 90 DAYS

Sample number	Haloether	Concentration (avg. of 3 runs), µg/mL	Avg. rel. std. dev., %	Percent change
90 M-1	CEVE	0	_[a]	_[a]
	BCIPE	11	1.4	+20
	BCEE	6.3	1.5	+11
	BCEXM	12	1.9	-14
	BPPE	5.8	0.6	+7.4
90 M-2	CEVE	0	_[a]	_[a]
	BCIPE	12	3.4	+30
	BCEE	6.5	3.5	+14
	BCEXM	13	3.9	-7.2
	BPPE	5.9	1.8	+9.3
90 M-3	CEVE	0	_[a]	_[a]
	BCIPE	12	0.9	+30
	BCEE	6.6	1.6	+16
	BCEXM	13	0.7	-7.2
	BPPE	5.9	0.1	+9.3

[a]Not determined.

TABLE 33. RESULTS OF ANALYSIS FOR ACETONE SOLUTION AFTER STORAGE FOR 90 DAYS

Sample number	Haloether	Concentration (avg. of 3 runs), µg/mL	Avg. rel. std. dev., %	Percent change
90 A-1	CEVE	19	13	+92[a]
	BCIPE	12	8.7	+21
	BCEE	5.8	9.4	-3.4
	BCEXM	15	11	-7.3
	BPPE	6.0	2.3	+11
90 A-2	CEVE	17	6.2	+72[a]
	BCIPE	11	4.1	+11
	BCEE	5.4	4.9	-10
	BCEXM	13	4.6	-19
	BPPE	5.9	1.4	+9.3
90 A-3	CEVE	15	6.7	+52[a]
	BCIPE	10	4.7	+1.0
	BCEE	5.6	5.4	-6.7
	BCEXM	12	6.5	-25
	BPPE	5.7	3.4	+5.6

[a]An unresolved impurity peak eluted as a hump on the trailing edge of the CEVE peak. This caused the computer to integrate both peaks together - giving very high values. The hump may be a degradation product of electron capturing impurities.

TABLE 34. COMPARISON OF ALL STORAGE TIMES

Haloether	Initial analysis (avg 3 runs), µg/mL	Percent recovery (avg 3 samples) 30 days, percent	60 days, percent	90 days, percent
	Acetone solution			
CEVE	9.9 ± 0.5	105 ± 3	107 ± 4	172 ± 15
BCIPE	9.9 ± 0.2	100 ± 2	103 ± 3	111 ± 6
BCEE	6.0 ± 0.2	100 ± 2	102 ± 3	93 ± 6
BCEXM	16.0 ± 0.6	100 ± 2	102 ± 3	83 ± 6
BPPE	5.4 ± 0.1	113 ± 15	94 ± 3	109 ± 3
	Methanol solution			
CEVE				
BCIPE	9.2 ± 0.5	105 ± 7	99 ± 2	130 ± 2
BCEE	5.7 ± 0.2	98 ± 2	96 ± 3	114 ± 2
BCEXM	14.0 ± 0.6	100 ± 2	100 ± 3	93 ± 2
BPPE	5.4 ± 0.1	111 ± 14	96 ± 4	109 ± 3

Note: Blanks indicate not determined.

CLASSIFICATION

These statistics show that CEVE is very unstable in methanol. In the initial analysis of the methanol solution, we were unable to arrive at an acceptable concentration for CEVE. The concentration of CEVE in methanol was a steadily decreasing value with time. This is due largely to the rapid hydrolysis of CEVE in methanol. By the time the 30 day samples were analyzed, the CEVE had hydrolyzed completely and we were unable to detect any CEVE. Inspection of the data in Table 34 seems to indicate that, except for CEVE, which has since been dropped from the study because of its volatility, the compounds are stable in both acetone and methanol.

There is some fluctuation in data of the samples over the varying time periods. This is attributed largely to the impurities in BCIPE and their decomposition and interference. The purest sample of BCIPE that could be obtained still contained over 30 electron-capturing impurities, many of which had retention times near those of the other haloethers. These impurities made the analysis very difficult. Because of these impurity interferences, we were unable to obtain any data regarding the growth of degradation peaks from the original haloether compounds. A sample chromatogram showing the elctron-capturing impurities in BCIPE is shown in Figure 7 (see page 25).

SIX TYPING LINES REMAIN

LAST LINE

CLASSIFICATION

SECTION 8

RESIN STUDIES

Studies were completed to evaluate the Ambersorb XE-340 and XAD-2 resins for use as concentrators. The two resins were Soxhlet extracted with acetontrile overnight; then Soxhlet extracted with methanol overnight. The resin was then stored in methanol. They were packed into columns (10 mm ID) to a depth of 6 cm. Buffered solutions (of pH 2, pH 7, and pH 10) were prepared in the manner described for the extraction studies (Section 5). One-liter portions of the buffers were then spiked with 100 µL of the concentrated haloether solutions and passed through the resin beds. The beds were then eluted using 150 mL of ethyl ether for the XAD-2 and 150 mL of acetone for the Ambersorb XE-340.

Both resins showed the ability to remove the haloethers from water. However, we were unable to strip the haloethers from the Ambersorb XE-340 using either acetone or methanol. The XAD-2 resin worked well on both counts, and the recovery data are presented in Tables 35-37 for pH values of 2, 7, and 10. Due to the high volatility of CEVE, we were unable to recover any appreciable amounts of the compound. Analysis of the data using the F test showed no significant variation in the percent recovery at any of the three pH values used.

TABLE 35. STATISTICAL DATA FOR XAD-2 RESIN AT pH 2

Ether	Percent recovered	Average percent recovered	Std. dev.	Rel. std. dev., %
CEVE[a]				
BCIPE #1	62.2			
#2	71.7	71.2	8.8	12.3
#3	79.7			
BCEE #1	40.4			
#2	47.4	45.0	4.0	8.9
#3	47.2			
BCEXM #1	59.3			
#2	67.3	67.9	9.0	13.3
#3	77.3			
BPPE #1	69.9			
#2	81.7	77.7	6.8	8.7
#3	81.6			

[a] Insufficient data for statistics.

TABLE 36. STATISTICAL DATA FOR XAD-2 RESIN AT pH 7

Ether		Percent recovered	Average percent recovered	Std. dev.	Rel. std. dev., %
CEVE[a]					
BCIPE	#1	58.0			
	#2	76.2	70.7	11.0	15.5
	#3	77.8			
BCEE	#1	43.8			
	#2	56.1	51.4	6.7	12.9
	#3	54.3			
BCEXM	#1	59.0			
	#2	69.8	68.9	9.5	13.7
	#3	77.9			
BPPE	#1	65.6			
	#2	67.2	71.8	9.4	13.1
	#3	82.7			

[a]Insufficient data for statistics.

TABLE 37. STATISTICAL DATA FOR XAD-2 AT pH 10

Ether		Percent recovered	Average percent recovered	Std. dev.	Rel. std. dev., %
CEVE[a]					
BCIPE	#1	80.9			
	#2	68.7	77.8	7.9	10.2
	#3	83.6			
BCEE	#1	54.8			
	#2	52.8	57.8	7.0	12.0
	#3	65.7			
BCEXM	#1	84.8			
	#2	66.9	77.8	9.6	12.3
	#3	81.6			
BPPE	#1	78.0			
	#2	69.2	75.1	5.1	6.7
	#3	78.0			

[a]Insufficient data for statistics.

In comparing the resin sorption method of sampling and analysis with the grab and extraction method, we see that each has its own advantages and disadvantages. Grab sampling requires only an adjustment to neutral pH and is therefore very simple in comparison with pumping an exact amount of sample through the resin tube. Neither method requires refrigeration. The resin method requires considerable preparation i.e., Soxhlet extraction and tube packing. The grab sampling, on the other hand, requires only a one gallon bottle. The resin tubes are smaller and would be easier and cheaper to ship than the gallon bottles which weigh about 9 pounds each.

The resin method seems to give recovery data equal to the grab and extraction method. Serious consideration should be given to this method as an alternative.

SECTION 9

COLUMN CHROMATOGRAPHY STUDIES

Column chromatography studies were conducted to find a chromatographic medium sufficient for the removal of potential interferences that may be encountered in actual industrial wastewaters.

Column Packed with Florisil

Four columns were packed with Florisil and eluted with 200 mL of varying concentrations of ethyl ether in petroleum ether according to the Method for Organochlorine Pesticides in Industrial Effluents (43).

Data for the recovery of the six haloethers from the Florisil columns are listed in Table 38. The samples were run simultaneously using a Hall Model 700 detector and a FID, as well as a Hall Model 310 detector. Table 38 provides the average recovery for the three detectors.

TABLE 38. AVERAGE RECOVERY PERCENT (THREE DETECTORS) OF HALOETHERS ON CHROMATOGRAPHIC COLUMN PACKED WITH FLORISIL AND ELUTED WITH 200 mL 6% ETHYL ETHER IN PETROLEUM ETHER

Ether	Average percent recovered (3 detectors)	Average standard deviation	Relative standard deviation, percent
CEVE	6.8	4.2	61.8[a]
BCIPE	82.1	2.7	3.3
BCEE	79.0	2.6	3.3
BCEXM	71.6	8.6	12.0
CPPE	78.5	4.7	6.0
BPPE	80.9	5.2	6.4

[a]Two detectors (not detected on FID due to solvent venting).

(43) Determination of Organochlorine Pesticides in Industrial Effluents. Federal Register, 38(125):17319, Part II, Appendix II, 29 June 1975.

Most of the haloethers elute in the 6% ethyl ether fraction, as shown in Table 38, with only a slight amount (10%) of BCEXM eluting in the second or 15% ethyl ether fraction. None of the haloethers were detected in the 50% ethyl ether fraction. Further studies showed that 300 mL of 6% ethyl ether in petroleum ether was sufficient to remove all (including BCEXM) of the haloethers from the column.

Column Packed with Silica Gel

Columns with 2 cm ID were slurry packed with 20 grams of 60-200 mesh silica gel. The haloether samples were then charged on the head of the column and eluted with varying concentrations (5, 10, 20, 30, and 50%) of methylene chloride in hexane.

An experiment was conducted with four identical samples charged on four columns. The FID analyses of the resulting fractions are shown in Table 39. Since the data were so erratic, the analyses were repeated. These results are shown in Table 40. Faced with another set of erratic data, it was decided to start again with a repeat experiment. The resulting fractions were analyzed with the FID (Table 41) and the Hall Model 700 detector (Table 42). The recovery of the six haloethers was very erratic and did not reproduce from one replicate to the other. Therefore, Florisil appeared to be the packing of choice for the sample cleanup. Because of the erratic data shown in Tables 39-42, the use of silica gel was not explored further as a column cleanup media. It was further concluded that 300 mL eluate of 6% ethyl ether in petroleum ether is needed to get complete release of all the haloethers from the Florisil.

TABLE 39. RECOVERY OF HALOETHERS ON CHROMATOGRAPHIC COLUMN PACKED WITH SILICA GEL AND ELUTED WITH METHYLENE CHLORIDE IN HEXANE - FIRST FID ANALYSIS

Haloether	Percent recovered			
	No. 1	No. 2	No. 3	No. 4
Using 5% $MeCl_2$ in Hexane				
CEVE	-	-	-	-
BCIPE	-	0.6	1.0	1.1
BCEE	3.4	8.4	14.5	-
BCEXM	0.4	-	5.4	5.3
CPPE[a]				
BPPE	100.7	101.1	100.3	100.5
Using 10% $MeCl_2$ in Hexane				
CEVE	-	-	-	-
BCIPE	4.9	2.9	7.4	19.0
BCEE	4.5	4.8	4.9	4.9
BCEXM	0.7	-	-	2.7
CPPE[a]				
BPPE	-	-	-	-
Using 20% $MeCl_2$ in Hexane				
CEVE	-	-	-	-
BCIPE	71.3	90.8	99.7	87.1
BCEE	53.7	80.4	107.8	79.5
BCEXM	-	-	-	-
CPPE[a]				
BPPE	-	-	-	-
Using 30% $MeCl_2$ in Hexane				
CEVE	-	-	-	-
BCIPE	1.9	1.8	5.4	2.5
BCEE	22.5	40.3	50.7	59.5
BCEXM	0.2	68.7	0.8	46.5
CPPE[a]				
BPPE	-	-	-	-
Using 50% $MeCl_2$ in Hexane				
CEVE	-	-	-	-
BCIPE	0.2	0.2	-	0.2
BCEE	-	-	-	-
BCEXM	43.3	27.6	8.6	19.9
CPPE[a]				
BPPE	-	-	-	-
Total Elution				
CEVE	-	-	-	-
BCIPE	78.3	96.3	113.5	109.9
BCEE	84.1	133.9	177.9	143.9
BCEXM	44.6	96.3	14.8	74.4
CPPE[a]				
BPPE	100.7	101.1	100.3	100.5

[a]Not included.

TABLE 40. RECOVERY OF HALOETHERS ON CHROMATOGRAPHIC COLUMN PACKED WITH SILICA GEL AND ELUTED WITH METHYLENE CHLORIDE IN HEXANE - SECOND FID ANALYSIS

Haloether	Percent recovered			
	No. 1	No. 2	No. 3	No. 4
Using 5% $MeCl_2$ in Hexane				
CEVE	-	-	-	-
BCIPE	-	0.5	1.0	1.0
BCEE	4.2	8.2	-	-
BCEXM	7.9	-	5.7	5.6
CPPE[a]				
BPPE	107.9	105.7	101.0	100.7
Using 10% $MeCl_2$ in Hexane				
CEVE	-	-	-	-
BCIPE	4.7	2.9	7.1	18.8
BCEE	4.2	4.7	4.7	4.8
BCEXM	-	-	-	-
CPPE[a]				
BPPE	-	-	-	-
Using 20% $MeCl_2$ in Hexane				
CEVE	-	-	-	-
BCIPE	68.4	88.9	96.5	86.6
BCEE	51.9	80.4	104.8	79.9
BCEXM	-	-	-	-
CPPE[a]				
BPPE	-	-	-	-
Using 30% $MeCl_2$ in Hexane				
CEVE	-	-	-	-
BCIPE	2.1	1.7	5.8	2.5
BCEE	22.7	40.0	51.6	61.0
BCEXM	-	73.2	0.8	50.6
CPPE[a]				
BPPE	-	-	-	-
Using 50% $MeCl_2$ in Hexane				
CEVE	-	-	-	-
BCIPE	0.2	0.3	-	-
BCEE	-	-	-	-
BCEXM	60.2	29.3	8.8	26.6
CPPE[a]				
BPPE	-	-	-	-
Total Elution				
CEVE	-	-	-	-
BCIPE	75.4	94.3	110.4	108.9
BCEE	83.0	133.3	161.1	145.7
BCEXM	68.1	102.5	15.3	82.8
CPPE[a]				
BPPE	107.9	105.7	101.0	100.7

[a]Not included.

TABLE 41. RECOVERY OF HALOETHERS ON CHROMATOGRAPHIC COLUMN PACKED WITH SILICA GEL AND ELUTED WITH METHYLENE CHLORIDE IN HEXANE - THIRD FID ANALYSIS

Haloether	Percent recovered			
	No. 1	No. 2	No. 3	No. 4
Using 5% $MeCl_2$ in Hexane				
CEVE	-	-	-	-
BCIPE	-	-	-	-
BCEE	-	-	-	-
BCEXM	-	-	-	-
CPPE	10.7	40.3	7.7	10.3
BPPE	6.4	39.6	5.5	7.0
Using 10% $MeCl_2$ in Hexane				
CEVE	-	3.5	-	-
BCIPE	-	-	-	27.2
BCEE	-	-	-	100.1
BCEXM	-	-	-	-
CPPE	65.7	36.2	46.5	-
BPPE	66.9	35.0	45.2	1.0
Using 20% $MeCl_2$ in Hexane				
CEVE	-	-	-	-
BCIPE	-	-	4.1	-
BCEE	-	-	-	-
BCEXM	-	-	-	-
CPPE	44.0	-	-	-
BPPE	44.5	1.4	-	-
Using 30% $MeCl_2$ in Hexane				
CEVE	-	-	-	-
BCIPE	-	80.8	58.6	66.6
BCEE	-	-	29.5	2.3
BCEXM	-	-	-	-
CPPE	-	-	-	-
BPPE	1.3	-	-	-
Using 50% $MeCl_2$ in Hexane				
CEVE	-	-	-	-
BCIPE	41.3	13.9	6.1	20.7
BCEE	-	65.7	36.8	74.8
BCEXM	-	-	-	-
CPPE	-	-	-	-
BPPE	1.6	0.7	-	-
Total Elution				
CEVE	-	3.5	-	-
BCIPE	41.3	94.7	68.8	114.5
BCEE	-	65.7	66.3	177.2
BCEXM	-	-	-	-
CPPE	120.4	76.5	54.2	10.3
BPPE	120.7	76.7	50.7	8.0

TABLE 42. RECOVERY OF HALOETHERS ON CHROMATOGRAPHIC COLUMN PACKED WITH SILICA GEL AND ELUTED WITH METHYLENE CHLORIDE IN HEXANE - (HALL MODEL 700)

Haloether	Percent recovered No. 1	No. 2	No. 3	No. 4
Using 5% $MeCl_2$ in Hexane				
CEVE	-	-	-	-
BCIPE	-	-	-	-
BCEE	-	-	-	-
BCEXM	0.1	0.1	-	0.1
CPPE	6.9	41.3	5.4	8.6
BPPE	4.1	31.9	4.3	4.9
Using 10% $MeCl_2$ in Hexane				
CEVE	-	8.5	0.3	-
BCIPE	-	-	-	27.2
BCEE	-	-	-	94.5
BCEXM	0.1	-	-	-
CPPE	59.6	33.2	48.8	1.0
BPPE	64.1	27.9	35.4	1.0
Using 20% $MeCl_2$ in Hexane				
CEVE	-	-	1.6	1.7
BCIPE	-	-	4.3	-
BCEE	-	-	0.1	-
BCEXM	0.1	-	0.1	-
CPPE	38.9	0.5	1.3	-
BPPE	38.9	1.1	0.4	-
Using 30% $MeCl_2$ in Hexane				
CEVE	1.7	0.3	-[a]	-
BCIPE	-	82.9	-[a]	68.1
BCEE	0.1	-	-[a]	4.1
BCEXM	0.2	-	-[a]	-
CPPE	0.4	0.7	-[a]	-
BPPE	0.4	-	-[a]	-
Using 50% $MeCl_2$ in Hexane				
CEVE	-	-	-	-
BCIPE	43.1	14.5	6.3	21.9
BCEE	2.5	65.1	35.9	76.2
BCEXM	0.1	0.1	-	-
CPPE	0.2	-	0.2	0.4
BPPE	0.7	0.6	0.2	0.2
Total Elution				
CEVE	1.7	8.8	1.9	1.7
BCIPE	43.1	97.4	10.6	117.2
BCEE	2.6	65.1	36.0	174.8
BCEXM	0.6	0.2	0.1	0.1
CPPE	106.0	75.7	55.7	10.0
BPPE	108.2	61.5	40.3	6.1

[a]Missing.

SECTION 10

APPLICATION OF METHOD TO WASTEWATER SAMPLES

Wastewater samples were obtained from a municipal secondary waste treatment plant and three industrial sites. Each of these four samples was divided into seventeen one-liter portions as shown in Table 43. The spiked samples were one-liter portions of wastewater spiked with 100 µL of a solution containing the concentrations of the six haloethers listed in Table 44. These concentrations are equal to 1,000 times the baseline noise for either the Hall electrolytic conductivity detector or the flame ionization detector, depending which was least sensitive for that particular haloether.

TABLE 43. DISTRIBUTION OF WASTEWATER SAMPLE PORTIONS

Sample	No. of 1-liter portions
Blank	1
Spiked as received for extraction	3
Spiked as received for XAD	3
Blank for XAD	1
Spiked storage 7 days at 4°C, for extraction	3
Spiked storage 7 days at 25°C, for extraction	3
Spiked storage 7 days at 4°C, for XAD	3

TABLE 44. CONCENTRATION OF HALOETHERS IN SPIKING SOLUTION

Haloether	Concentration, mg/mL
CEVE	1.17
BCEE	0.97
BCIPE	0.54
BCEXM	1.38
CPPE	0.3
BPPE	0.14

The samples were extracted with three 60 mL portions of methylene chloride. These three portions were combined, dried with sodium sulfate, concentrated with hexane, and eluted from Florisil using 300 mL of a solution containing 6% ethyl ether in petroleum ether. Then, the samples were again concentrated using K-D evaporator, the volume adjusted to 10 mL, and the samples were ready for analysis. Table 43 shows that the XAD resin sorption method was also used to prepare samples fr analysis. In this procedure the wastewater samples were spiked and run through the resin procedure as described in Section 8. The samples were then either stripped and analyzed immediately or stored for 7 days at 4°C and then stripped and analyzed.

All of the analyses were done using the Hall electrolytic conductivity detector with a column packed with 3% SP-1000. The municipal wastewater was the first to be analyzed. The results of these analyses are shown in Table 45. This table shows results based on both peak area and peak amplitude as determined by a Hewlett-Packard computer integrator.

TABLE 45. RECOVERY OF HALOETHERS FROM WASTEWATER FROM MUNICIPAL SECONDARY WASTE TREATMENT PLANT USING COLUMN PACKED WITH SP-1000 AND HALL ELECTROLYTIC CONDUCTIVITY DETECTOR

		Based on peak area		Based on peak amplitude	
Sample condition	Haloether	Percent recovered	Rel. std. dev., %	Percent recovered	Rel. std. dev., %
Spiked, as received, extracted (3 samples)	CEVE	9.28	32.5	16.66	4.3
	BCIPE	72.17	2.9	67.86	14.3
	BCEE	70.67	7.7	64.59	17.5
	BCEXM	75.36	4.4	68.36	19.2
	CPPE	80.93	11.6	73.17	16.2
	BPPE	92.28	55.7	81.26	8.8
Spiked, as received, XAD-2 (3 samples)	CEVE	8.59	35.6	13.31	10.5
	BCIPE	65.33	12.0	58.6	4.6
	BCEE	51.58	11.5	47.33	5.6
	BCEXM	64.58	13.6	55.95	4.1
	CPPE	63.30	20.1	64.39	0.3
	BPPE	89.60	51.6	73.81	5.5
Spiked, storage at 25°C, extracted (3 samples)	CEVE	21.43	22.5	21.57	9.3
	BCIPE	85.00	6.4	60.77	7.6
	BCEE	83.91	11.1	58.29	7.1
	BCEXM	85.06	8.2	59.58	9.3
	CPPE	97.50	14.4	64.59	7.1
	BPPE	159.85	60.9	71.95	7.3
Spiked, storage at 4°C, (3 samples)	CEVE	11.94	16.1	20.32	2.8
	BCIPE	74.61	10.1	73.73	1.2
	BCEE	71.17	10.0	71.32	1.9
	BCEXM	73.35	6.4	74.25	1.3
	CPPE	78.22	14.4	76.72	2.0
	BPPE	85.49	9.7	75.62	1.2

No final conclusions could be drawn from Table 45 because of the unresolved question of peak areas versus amplitudes. Therefore, an experiment was devised to determine which method of measurement gave more consistent results. The average results for five analyses of a standard sample with the Hall detector are listed in Table 46. An improvement of the relative standard deviation was noted in almost all cases for the results calculated using amplitudes as compared to those calculated using areas. Therefore, it was decided to use peak amplitude in the rest of the analyses.

TABLE 46. AVERAGE RESULTS FOR FIVE ANALYSES OF HALOETHER STANDARD ANALYZED ON COLUMN PACKED WITH SP-1000 AND USING HALL ELECTROLYTIC CONDUCTIVITY DETECTOR

Haloether	Concentration, µg/mL	Relative standard deviation, %	
		Based on peak area	Based on peak amplitude
CEVE	23.4	10.5	4.0
BCIPE	10.8	3.9	2.2
BCEE	19.4	3.2	1.4
BCEXM	27.6	4.4	2.4
CPPE	6.0	7.8	2.2
BPPE	2.8	17.8	3.6

After the decision was made to use peak amplitude, the rest of the wastewater analyses were completed. The blank samples (except for source #3) had no response on the Hall detector at retention times which interfered with the haloethers. Source #3 had several interferences which could not be removed with the Florisil cleanup. These interferences were so large and eluted so close to some of the haloethers that they overshadowed all compounds near them. The data for recovery of the haloethers from the wastewaters are shown in Table 47. A "t" test was conducted on the data from the three sites; the values for these sets are listed in Table 48. The "t" values were generated by the following comparison.

The mathematical formula used in calculating the "t" values was:

$$t = \frac{|X_1 - X_2|}{\sqrt{\frac{S_1^2 + S_2^2}{3}}}$$

TABLE 47. PERCENT RECOVERIES OF HALOETHERS FROM INDUSTRIAL AND MUNICIPAL WASTEWATER (DETERMINED BY PEAK AMPLITUDE) USING COLUMN PACKED WITH SP-1000 AND HALL ELECTROLYTIC DETECTOR (AVERAGE OF THREE SAMPLES)

Sample	As received		Stored at 25°C for 1 week		Stored at 4°C for 1 week		XAD-2		XAD-2 stored for 1 week	
	Percent recovered	Percent RSD	Percent recovered	Percent RSD	Percent recovered	Percent RSD	Percent recovered	Percent RSD	Percent recovered	Percent RSD
Industrial #1										
BCIPE	68.0	0.4	70.9	4.6	71.2	3.2	76.9	1.4	72.6	2.6
BCEE	56.5	0.6	67.1	5.3	59.8	5.8	66.4	3.1	61.3	3.8
BCEXM	60.2	2.0	70.7	6.3	67.6	5.5	69.1	2.5	63.8	5.2
CPPE	73.3	2.8	74.1	3.0	77.1	2.7	77.5	1.8	75.4	2.6
BPPE	82.9	3.2	79.8	2.6	89.4	4.5	79.2	1.2	84.4	4.7
Industrial #2										
BCIPE	62.9	1.2	64.6	3.0	65.3	3.4	76.2	2.4	77.7	2.9
BCEE	51.2	1.7	53.0	5.6	52.7	4.2	64.8	1.2	66.5	2.1
BCEXM	51.4	1.6	54.3	4.1	56.0	5.8	69.3	3.0	70.7	2.0
CPPE	70.1	0.4	71.4	1.4	72.5	1.4	77.3	3.5	77.3	1.7
BPPE	71.7	1.0	72.1	0.2	73.3	1.4	76.3	1.7	77.8	1.5
Industrial #3[a]										
Municipal #1										
BCIPE	67.9	14.3	60.8	7.6	73.7	1.2	58.6	4.6	63.8	2.3
BCEE	64.6	17.3	58.3	7.1	71.3	1.9	47.3	5.6	60.6	6.4
BCEXM	68.4	19.2	59.6	9.3	74.3	1.3	56.0	4.1	61.1	4.3
CPPE	73.2	16.2	64.6	7.1	76.7	2.0	64.4	0.3	68.8	4.1
BPPE	81.3	8.8	72.0	7.3	75.6	1.2	73.8	5.5	74.9	5.1

[a]Unable to obtain recovery data because of interferences.

TABLE 48. "t" VALUES FOR THREE SETS OF WASTEWATER SAMPLES

Sample	Haloether	A/B	B/C	A/C	A/D	D/E
Industrial #1	BCIPE	1.52	0.23	2.39	13.85	3.41
	BCEE	5.08	2.52	1.63	8.06	2.82
	BCEXM	3.90	0.92	3.30	7.41	2.46
	CPPE	0.46	1.71	2.22	2.88	1.58
	BPPE	1.57	3.68	2.33	2.23	2.20
Industrial #2	BCIPE	1.43	0.41	1.76	11.53	0.89
	BCEE	0.99	0.14	1.08	19.77	0.76
	BCEXM	2.15	0.75	2.38	4.84	0.97
	CPPE	2.16	1.33	3.91	4.57	0
	BPPE	0.98	2.01	2.23	8.22	1.72
Municipal	BCIPE	1.14	4.42	1.03	1.60	2.93
	BCEE	0.91	5.17	1.03	2.60	4.90
	BCEXM	1.07	4.22	0.65	2.39	0.57
	CPPE	1.16	4.69	0.51	1.28	0.50
	BPPE	1.81	1.17	1.36	1.57	0.34

Note: A/B: Initial (A) to 25°C (B)
A/C: Initial (A) to 4°C (C)
B/C: 25°C (B) to 4°C (C)
A/D: Initial (A) to XAD-2 (D)
D/E: XAD-2 (D) to XAD-2/week (E)

where X_1 and X_2 are the values of the two samples being compared and S_1 and S_2 are the standard deviation of each. If the "t" value is ≥2.776, then there is a 95% probability that the two data points are not from the same population. If the "t" value is ≥8.610, the probability of the two data points being from different populations is 99.9%. Observation of the data from Table 48 seems to indicate that, on the whole, there is not much difference in the samples extracted initially or stored at 25°C and 4°C. There is, however, a statistical difference in the samples analyzed using extraction as opposed to those using the XAD-2 resin. For the two industrial waters, the data indicate XAD concentration results in better recoveries than methylene chloride extraction for most of the haloethers.

The method application study determined the effectiveness of the elements in the Phase I research. Experience indicates that most elements of the study have been resolved. The 3% SP-1000 on Supelcoport performed without failure. The Hall detector proved to be a reliable system when proper precautions were observed, and the current GC temperature program gives well defined results within an efficient time frame. Interferences, however, may prove to be a significant limitation to the application of the

method. Many non-halogenated compounds were identified in wastewater samples by GC/MS which gave significant peaks on the Hall detector spectra. Wastewater #3 of this study, in particular, confirmed potential interference problems with the extraction-cleanup procedure/detector system used. Since both liquid/liquid extraction and XAD resin sorption give good recovery data, further research could determine if XAD resins could reduce the interferences which were observed in various wastewater types.

It has been shown that the haloethers have no special storage problems. However, special storage is indicated for biologically active wastewaters because of possible composition changes which may interfere with haloether detection.

REFERENCES

1. Durkin, P. R., P. H. Howard, and J. Saxena. Investigation of Selected Potential Environmental Contaminants: Haloethers. EPA 560/2-75-006, U.S. Environmental Protection Agency, Washington, D.C., September 1975. 178 pp.

2. Böhme, H. and K. Sell. The Hydrolysis of Halogenated Ethers and Thio Ethers in Water-Dioxane Mixtures. Chem. Ber., 81:123-130, 1973.

3. Van Duuren, B. L., C. Katz, B. M. Goldschmidt, K. Frenkel, and A. Sivak. Carcinogenicity of Halo-ethers. II. Structure - Activity Relation of Analogs of Bis(chloromethyl) ether. J. Nat. Cancer Inst., 48:1431-1439, 1972.

4. Salomaa, P., A. Kankaanpera, and M. Lajuneh. Protolytic Cleavage of Vinyl Ethers. General Acid Catalysis, Structural Effects and Deuterium Solvent Isotope Effects. Acta. Chem. Scand., 20(7):1790-1801, 1966.

5. Brown, S. L., F. Y. Chan, J. L. Jones, D. H. Liu, K. E. McCaleb, T. Mill, K. N. Sapios, and D. E. Schendal. Research Program on Hazard Priority Ranking of Manufactured Chemicals (Chemicals 61-79). NSF-RA-E-75-190D, National Science Foundation, Washington, D.C., April 1975. 198 pp.

6. Roberts, R. F., Jr. Catalytically Cleaving Dichloroisopropyl Ether. U.S. Patent 3,723,544 (to Dow Chemical Co.), 27 March 1973.

7. Van Duuren, B. L., A. Sivak, B. M. Goldschmidt, C. Katz, and S. Melchionne. Carcinogenicity of Halo-ethers. J. Nat. Cancer Inst., 43:481, 1969.

8. Van Duuren, B. L. Carcinogenic Epoxides, Lactones and Halo-ethers and Their Mode of Action. Ann. New York Acad. Sci. 163:633-651, 1969.

9. Bis(chloromethyl) Ether Can Form Spontaneously. Chem. Eng. News, 51(2):13, 8 January 1973.

10. Frankel, L. S., K. S. McCallum, and L. Collier. Formation of Bis(chloromethyl) Ether from Formaldehyde and Hydrogen Chloride. Environ. Sci. Technol., 8(4):356-359, 1974.

CLASSIFICATION

11. Kallos, G. J. and R. A. Solomon. Formation of Bis(chloromethyl) Ether in Simulated Hydrogen Chloride-Formaldehyde Atmospheric Environments. Amer. Ind. Hyg. Assoc. J., 34:469-473, November 1973.

12. Tou, J. C. and G. J. Kallos. Kinetic Study of the Stabilities of Chloromethyl Methyl Ether and Bis(chloromethyl) Ether in Humid Air. Anal. Chem., 46(12):1866-1869, 1974.

13. Tou, J. C., L. B. Westover, and L. F. Sonnabend. Kinetic Study of Bis(chloromethyl) Ether Hydrolysis by Mass Spectrometry. J. Phys. Chem., 78(11):1096-1098, 1974.

14. Tou, J. C. and G. J. Kallos. Study of Aqueous HCl and Formaldehyde Mixtures for Formation of Bis(chloromethyl) Ether. Amer. Ind. Hyg. Assoc. J., 35:419-422, July 1974.

15. Tou, J. C., L. B. Westover, and L. F. Sonnabend. Analysis of a Non-Crosslinked, Water Soluble Anion Exchange Resin for the Possible Presence of Parts Per Billion Level of Bis(chloromethyl) Ether. Amer. Ind. Hyg. Assoc. J., 36:374-378, May 1975.

16. Marceleno, T. and P. J. Bierbaum. A Preliminary Report on the Formation and Detection of Bis-Chloromethyl Ether in the Industrial and Medical Environment. Presented at American Industrial Hygiene Association Conference, Miami, Florida, 12-17 May 1974.

17. Alvarez, M. and R. T. Rosen. Formation and Decomposition of Bis(chloromethyl) Ether in Aqueous Media. Int. J. Environ. Anal. Chem., 4:241-246, 1976.

18. Rosen, A. A., R. T. Skeel, and M. B. Ettinger. Relationship of River Water Odor to Specific Organic Contaminants. J. Water Pollut. Contr. Fedr., 35(6):777-782, 1963.

19. Frilous, J. Petrochemical Wastes as a Pollution Problem in the Lower Mississippi River. Paper submitted to Senate Subcommittee on Air and Water Pollution, 5 April 1971.

20. Industrial Pollution of the Lower Mississippi River in Louisiana. PB 229 814, U.S. Environmental Protection Agency, Region VI, Dallas, Texas. April 1972. 154 pp.

21. Kleopfer, R. D, and B. J. Fairless. Characterization of Organic Components in a Municipal Water Supply. Environ. Sci. Technol., 6(12):1036-1037, 1972.

22. Analytical Report New Orleans Area Water Supply Study. EPA 909/9-75-003, 1975. 90 pp. U.S. Environmental Protection Agency, Region VI, Dallas, Texas.

CLASSIFICATION

23. Webb, R. G., A. W. Garrison, L. H. Keith, and J. M. McGuire. Current Practice in GC-MS Analysis of Organics in Water. EPA-R-73-277, U.S. Environmental Protection Agency, Athens, Georgia, August 1973. 94 pp.

24. Manwaring, J. F., W. M. Blankenship, L. Miller, and F. Voigt. Bis(chloroethyl) Ether in Drinking Water - Its Detection and Removal. J. Amer. Water Works Assoc., 69:210-213, April 1977.

25. Dressman, R. C., J. Fair, and E. F. McFarreh. Determinative Method for Analysis of Aqueous Sample Extracts for Bis(2-Chloro)Ethers and Dichlorobenzenes. Environ. Sci. Technol., 11(7):719-721, 1977.

26. Berck, B. Determination of Fumigant Gases by Gas Chromatography. J. Agr. Food Chem., 113:373-377, 1965.

27. Collier, L. Determination of Bischloromethyl Ether in the ppb Level in Air Samples by High Resolution Mass Spectroscopy. Environ. Sci. Technol., 6(10):930-932, 1972.

28. Shadoff, L. A., G. J. Kallos, and J. S. Woods. Determination of Bis(chloromethyl) Ether in Air by Gas Chromatography - Mass Spectrometry. Analytical Chemistry, (45(14): 2341-2344, 1973.

29. Ellgehausen, D. Determination of Volatile Toxic Substances in the Air by Means of a Coupled Gas Chromatograph - Mass Spectrometer System. Analytical Letters, 8(1):11-23, 1975.

30. Sawicki, E. Bis(chloromethyl) Ether (Bis-CME) in Air Analytical Method. Health Lab Sci., 12:403-406, 1975.

31. Pellizzari, E. D., B. H. Carpenter, J. E. Bunch, and E. Sawicki. Collection and Analysis of Trace Organic Pollutants in Ambient Atmospheres - Techniques for Evaluating Concentration of Vapors by Sorbent Media. Environ. Sci. Technol., 9(6):552-555, 1975.

32 Pellizzari, E. D., B. H. Carpenter, and J. E. Bunch. Collection and Analysis of Trace Organic Vapor Pollutants in Ambient Atmospheres, Thermal Desorption of Organic Vapors from Solid Media. Environ. Sci. Technol., 9(6)556-560, 1975.

33. Frankel, L. S. and R. F. Black. Automatic Gas Chromatographic Monitor for the Determination of Parts-Per-Billion Levels of Bis(chloromethyl) Ether. Anal. Chem., 48(4): 732-737, 1976.

34. Pellizzari, E. D., J. E. Bunch, R. E. Berkley, and J. McRae. Collection and Analysis of Trace Organic Vapor Pollutants in Ambient Atmospheres, The Performance of a Tenax-GC Cartridge Samples for Hazardous Vapors. Analytical Letters, 9(1):45-63, 1976.

35. Evans, K. P., A. Mathias, N. Mellar, and R. Selvester. Detection and Estimation of Bis(chloromethyl) Ether in Air by Gas Chromatography - High Resolution Mass Spectrometry. Anal. Chem., 47(6):821-824, 1975.

36. NIOSH Analytical Methods for Set V. NIOSH-SCP V, National Institute for Occupational Safety and Health, Cincinnati, Ohio, December 1976. 43 pp.

37. Sherman, P. L., A. M. Kemmer, L. Metcalf, and H. D. Toy. Environmental Monitoring Near Industrial Sites: β-Chloroethers. EPA 56/6-78-003, U.S. Environmental Protection Agency, Washington, D.C., 1978. 271 pp.

38. Solomon, R. A. and G. J. Kallos. Determination of Chloromethyl Methyl Ether and Bis Chloromethyl Ether in Air at the Parts Per Billion Level by Gas-Liquid Chromatography. Anal. Chem., 47(6)955-957, 1975.

39. Solomon, R. A. Detection of Chloromethyl Methyl Ether or Bischloromethyl Ether, U.S. Patent 3,944,389 (to Dow Chemical Co.), 16 March 1976.

40. Sawicki, E. Analytical Method for Chloromethyl Methyl Ether (CMME) and Bischloromethyl Ether (BCME). Health Lab Sci., 13:78-81, 1976.

41. Sampling and Analysis Procedures for Screening of Industrial Effluents for Priority Pollutants, U.S. Environmental Protection Agency, Cincinnati, Ohio, April 1977.

42. Deinzer, M., R. Melton, and D. Mitchell. Trace Organic Contaminants in Drinking Water; Their Concentration by Reverse Osmosis. Water Res., 9:799-805, 1975.

43. Determination of Organochlorine Pesticides in Industrial Effluents. Federal Register, 38(125):17319, Part II, Appendix II, 29 June 1975.

APPENDIX A

METHOD FOR SAMPLING AND ANALYSIS

During the first year of this contract, a complete method was developed for the sampling and analysis of haloether in water and wastewater. The method involves a liquid-liquid extraction using methylene chloride, a solvent exchange with hexane, a Florisil-column chromatographic cleanup procedure, and subsequent analysis by gas chromatography using an electrolytic conductivity detector. A detailed description of this method is provided below.

Scope and Application

This method covers the determination of the following halogenated ethers in wastewaters:

- bis(2-chloroisopropyl) ether (BCIPE)
- bis(2-chloroethyl) ether (BCEE)
- bis(2-chloroethoxy) methane (BCEXM)
- 4-chlorophenyl phenyl ether (CPPE)
- 4-bromophenyl phenyl ether (BPPE)

Summary

This method offers an alternative to the high cost and technical expertise required for the analysis of haloethers by gas chromatography/mass spectrometry. The procedure involves a liquid-liquid extraction using methylene chloride and a column chromatographic cleanup procedure to remove potential interferences. The samples are then analyzed by gas chromatography using an electrolytic conductivity detector.

Apparatus and Reagents Required

For sample extraction, the following are required:

- 2,000-mL separatory funnel with Teflon stopcock
- 8-ounce Boston round bottle (glass)
- 4-dram vials (glass) and caps with conical polyethylene liners

- Funnel (60-mm diameter)
- Glass beads (2-mm diameter)
- Aluminum foil
- Kuderna-Danish (K-D) glassware with three-ball (micro) Snyder column, 500-mL evaporation flask, and 10-mL receiver ampule
- Extracting solvent - methylene chloride, "distilled in glass"
- Sodium sulfate - (ACS) granular, anhydrous (400°C for 4 hours

For chromatographic cleanup, the following are required:

- Florisil - 60/100 mesh
- Chromatographic columns - 11 mm ID x 300 mm long with 250-ml reservoir (KIMAX) with removal Teflon stopcocks
- Glass wool
- Kuderna-Danish evaporators with three-ball (macro) Snyder column, 500-mL evaporation flask, and 10-mL receiver ampule
- 4-dram vials (glass) and caps with conical polyethylene liners
- Septum-capped, glass, sample vials
- Sodium sulfate - (ACS) granular, anhydrous (400°C for 4 hours)
- Petroleum ether - "distilled in glass"
- Ethyl ether - (ACS) reagent grade
- Hexane - "distilled in glass"
- Lauric acid - reagent grade
- Sodium hydroxide - (ACS) reagent grade

For sample analysis, the following are required:

- Gas chromatograph - temperature programmable
- Detector - electrolytic conductivity
- Glass column - 2.1 mm ID x 1.8 m long
- Column packing - 3% SP-1000 on 100/120-mesh Supelcoport
- 10-µl syringe
- Carrier and auxilliary gases - helium and hydrogen, pure grades, to preserve column life and avoid interferences
- Haloethers standards - Commercial sources of haloether are listed below:

Compound	Commercial source
BCIPE	Monsanto Research Corporation, Dayton, Ohio 45407
BCEE	RFR Corp., Hope, Rhode Island 02831
BCEXM	Pfaltz & Bauer, Stamford, Conn. 06902
CPPE	RFR Corp., Hope, Rhode Island 02831
BPPE	Pflatz & Bauer, Stamford, Conn. 06902

- Ethanol - absolute (95%)
- Deionized water

Sampling and Preservation Procedure

Collect samples in one-liter glass containers having an inert liner (Teflon) incorporated in the cap. Prewash and solvent rinse the containers prior to sampling to prevent interferences. Follow conventional sampling practices.

Preserve the samples by sealing the bottle lids with a plastic tape and icing for shipment.

Sample Extraction Procedure

(1) Transfer a measured 1,000 mL of sample from the container to a two-liter separatory funnel. Discard the balance of the water from the container.

(2) Add 60 mL of the extracting solvent (methylene chloride) to the sample container and shake vigorously to rinse the bottle thoroughly. Transfer the solvent to the separatory funnel and shake the separatory funnel vigorously for 2 minutes.

(3) Allow the two phases to separate and draw the bottom (methylene chloride) layer into an 8-ounce Boston round bottle.

(4) Repeat Steps (2) and (3) two more times.

(5) Plug a standard laboratory funnel with glass wool and fill with approximately 40 mm of anhydrous, granular sodium sulfate.

(6) Pass the collected fractions through the sodium sulfate and collect in a 500-mL K-D flask.

(7) Rinse the 8-ounce Boston round bottle with approximately 50 mL of methylene chloride, pass it through the sodium sulfate, and collect in the 500-mL K-D flask.

(8) Place two glass beads into the flask, attach the three-ball Synder column to the flask, and place the lower half of the ampule in a steam bath.

(9) Insulate the K-D flask with aluminum foil to complete the evaporation in approximately 10-15 minutes.

(10) When the volume of the methylene chloride in the flask reaches approximately 10 mL, pour 50 mL of hexane in the top of the Snyder column. Be sure that there is a good washing of the walls of the Snyder column when the hexane passes down to the flask.

(11) Evaporate until the ampule is nearly dry. Drain the condensed vapors from the column into the cooled flask to obtain a final volume of approximately 6 mL.

(12) Rinse the Snyder column and walls of the K-D flask with an additional 1 mL of hexane.

(13) Remove the Snyder column and flask from the ampule.

(14) Transfer the concentrate to a 4-dram vial. Rinse the ampule with 1 mL of hexane and also transfer to the vial. Cap and seal the vial, and store in a cool, dark place to await column chromatography (volume at this point will equal ~8 mL).

Quantitation Procedure

Complete the quantitative measurements using gas chromatography with an electrolytic conductivity detector at the conditions listed below:

Item	Value/description
Carrier gas	Helium at 40 mL/min
Temperature program	60°C with 2 min post-script, then 8°C/min to 230°C with a 4-min hold
Column and packing	1.8 m x 2.1 mm ID glass packed with 3% SP-1000 on 100/200 mesh Supelcoport
Injection port temperature	250°C
Detector conditions	Tracor Model 700 Hall electrolytic conductivity detector or equivalent halogen selective detector. Furnace temperature at 900°C; transfer line temperature at 250°C. Absolute ethanol (95%) electrolyte at 0.3 mL/min.

CLASSIFICATION

Take the vials containing the samples and transfer the contents of each to a 10-mL volumetric flask. Rinse each vial with a total of 1 mL of hexane, transfer to flask and rinse again (rinses should equal ∿1 mL). Dilute each sample to exactly 10 mL using more hexane. Transfer the contents to each flask into septum-capped vials for gas chromatography and possible column chromatography.

Dilute the standard solutions containing haloethers in the concentrations shown below, by injecting 80 µL into 4 mL of hexane. The dilute solution is the gas chromatography standard and is 20 times baseline noise.

Haloether	Concentration, µg/mL
BCIPE	120
BCEE	70
BCEXM	50
CPPE	300
BPPE	150

The above concentrations are equal to 1,000 times the baseling noise for each compound on the Tracor Model 700 Hall electrolytic conductivity detector.

Procedure for Removal of Interference

Remove interference by Florisil column adsorption chromatography using the following procedure which has been taken from the "Method for Organochlorine Pesticides in Industrial Effluents" (43).

Place a charge of activated Florisil (weight determined by lauric acid value as described in Appendix B) in a glass chromatography column. After settling the Florisil by tapping the column, add about 15 mm of granular, anhydrous sodium sulfate to the top of the Florisil.

Pre-elute the column, after cooling, with 50-60 mL of petroleum ether. Discard the eluate. Just prior to exposure of the sulfate layer to air, quantitatively transfer the sample exact (either the contents of the 4-dram vial or the contents of the 10-mL volumetric flask) onto the column by decantation and subsequent petroleum ether washings. Charge eluate to 300 mL of 6% ethyl ether in petroleum ether. Adjust the elution rate to 5 mL/min and collect the eluate in a 500-mL K-D flask equipped with a 10-mL ampule.

Concentrate the eluate to approximately 6 mL in a K-D evaporation system using a steam bath, transfer to a 10-mL volumetric flask with subsequent rinsings, and dilute to exactly 10 mL.

CLASSIFICATION

CLASSIFICATION

Transfer to a septum-capped vial, and analyze by gas chromatography.

Quality Assurance Practice

Use standard quality assurance practices with this method. Collect field replicates to validate the precision of the sampling technique. Analyze laboratory replicates to validate the precision of the analysis. Analyze fortified samples to validate the accurracy of the analysis.

Calculations and Reporting

Determine the concentration in the sample according to the following formula:

$$\text{microgram/liter} = \frac{(A)\ (B)\ (Vt)}{(Vi)\ (Vs)}$$

where A = ng standard/standard area, integrator counts or cm^2

B = sample aliquot area, integrator counts or cm^2

Vt = volume of total extract, mL

Vi = volume of extract injected, µ

Vs = volume of water extracted, ℓ

Report results in micrograms per liter without corrections for recovery data. When duplicate and spiked samples are analyzed, report all data obtained.

SIX TYPING LINES REMAIN

LAST LINE

CLASSIFICATION

APPENDIX B

STANDARDIZATION OF FLORISIL

This rapid method for determining the adsorptive capacity of Florisil is based on the adsorption of lauric acid from hexane solution. An excess of lauric acid is used and the amount not adsorbed is measured by alkali tritration. The weight of lauric acid adsorbed is used to calculate, by simple proportion, the equivalent quantities of Florisil for batches having different adsorptive capacities.

Apparatus Required

(1) 25-mL buret with 1/10 mL graduations

(2) Erlenmeyer flasks - 125 mL narrow mouth and 25 mL glass stoppered

(3) Pipette - 10 mL and 20 mL transfer type

(4) 500-mL volumetric flasks

Reagents and Solvents Required

(1) Ethyl alcohol - USP or absolute, neutralized to phenolphthalein

(2) Hexane - "distilled in glass"

(3) Lauric acid - purified, CP

(4) Lauric acid solution prepared by transferring, 10,000 gram lauric acid to a 500-mL volumetric flask, dissolving in hexane, and diluting to 500 mL (1 mL = 20 mg)

(5) Phenolphthalein Indicator - dissolve 1 gram in alcohol and dilute to 100 mL

(6) Sodium hydroxide - dissolve 20 grams of NaOH (pellets, reagent grade) in water and dilute to 500 m: (lN). Dilute 25 mL of lN NaOH to 500 mL with water (0.05N). Standardize as follows: Weigh 100-200 mg lauric acid into 125 mL Erlenmeyer flask; add 50 mL of neutralized ethyl alcohol and 3 drops phenolphthalein indicator; titrate to permanent end point; calculate mg lauric acid/mL of 0.05N NaOH (about 10 mg/mL).

Procedure

(1) Transfer 2.000 gram Florisil to 25-mL glass-stoppered Erlenmeyer flasks. Cover loosely with aluminum foil and heat overnight at 130°C. Stopper, cool to room temperature, add 20.0 mL lauric acid solution (400 mg), stopper, and shake occasionally for 15 minutes. Let absorbant settle and pipette 10.0 mL of supernatant into 125-mL Erlenmeyer flask. Avoid inclusion of any Florisil.

(2) Add 50 mL of neutral alcohol and 3 drops indicator solution; titrate with o.05N to a permanent end point.

Calculation of Lauric Acid Value and Adjustment of Column Weight

(1) Calculate the amount of lauric acid adsorbed on Florisil as follows:

lauric acid value = mg lauric acid/gram of Florisil
= 200 - [(mL required for titration)
x (mg lauric acid/,1 0.05N NaOH)]

(2) To obtain an equivalent quantity of any batch of Florisil, divide 110 by lauric acid value for that bath and multiply by 20 g.